

**Report of the
Federal Advisory Committee
on
Detection and Quantitation Approaches and Uses
in
Clean Water Act Programs**

Submitted to the
US Environmental Protection Agency

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ACKNOWLEDGMENTS

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Dear Administrator Johnson:

We are pleased to present to you the Final Report of the Federal Advisory Committee on Detection and Quantitation Approaches and Uses in Clean Water Act Programs. This report responds to the charter from the US Environmental Protection Agency to “provide advice and recommendations on approaches for the development of detection and quantitation procedures and uses of these procedures in Clean Water Act programs.”

Our Committee included balanced representation from states, industry, environmental laboratories, public utilities and the environmental community as well as EPA’s Director of Engineering and Analysis Division. What brought the members of our Committee to the table and kept us hard at work for two and a half years was a common desire to improve federally-approved analytical procedures for determining Detection and Quantitation Limits and to reach agreement on the uses of the results.

We tackled difficult policy and technical questions. We agreed by consensus on many important issues and expect EPA will move these recommendations forward. We put other issues on the table which we all agreed are important but which we could not reach consensus within the time available. In these cases, we have provided you with the full array of opinions on the Committee so you will have the benefit of our deliberations. We urge EPA to address these issues at the same time it considers our consensus recommendations.

We would like to thank the Office of Water for affording our Committee the opportunity to address these important issues and for providing significant resources for our work, including funding the Pilot Study which was instrumental in developing a recommendation on a single laboratory procedure for detection and quantitation. We also appreciate the outstanding support that EPA staff provided throughout our deliberations.

We respectfully request a formal response to our recommendations.

Sincerely,

Members, Federal Advisory Committee on Detection and Quantitation Approaches and Uses in Clean Water Act Programs

TABLE OF CONTENTS

ACRONYMS

Executive Summary	i
-------------------------	---

TO THE READER	vi
---------------------	----

CHAPTER 1 – Purpose of the Committee and Committee Process. . . 1

1. Background	1
2. Situation Assessment	1
3. Creation of the Committee	1
4. Committee Process	2
5. Definitions of Detection and Quantitation	2

CHAPTER 2 – DATA QUALITY OBJECTIVES AND MEASUREMENT QUALITY OBJECTIVES 5

1. Introduction	5
2. Recommendations and Decisions on Data Quality Objectives	6
3. Recommendations and Decisions on Measurement Quality Objectives for Measurements used in NPDES Compliance Testing	8
4. Measurement Quality Objectives for Clean Water Act Uses	13

CHAPTER 3 – Procedures for Detection and Quantitation 15

1. Introduction	15
2. What The Committee Needs A Procedure To Do	16
3. Additional Requirements Based on Contemplated Uses of Detection and Quantitation in the Clean Water Act Program	17
4. Pilot Study Design	17
5. Pilot Study	18
6. Committee Decision-Making Process on a Single Laboratory Detection and Quantitation Procedure	20
7. Recommendations and Decisions on Procedure Verification	20
8. Decision on a Single Laboratory Procedure	29
9. Determining a National Quantitation Limit	35

CHAPTER 4 –USES OF DETECTION AND QUANTITATION IN CLEAN WATER ACT PROGRAMS. . 39

1. Introduction	39
2. Removal of a National Detection Limit From Uses Decisions	43
3. Establishing NPDES Permit Conditions and Determining Compliance	45
4. Alternative Test Procedures Program Compliance	52
5. Great Lakes Initiative Compliance	53

CHAPTER 5 – MATRIX EFFECTS.....54

1. Introduction	54
2. Matrix Effects: Discussion and Decisions	55

CHAPTER 6 – RECOMMENDATIONS ON OTHER ISSUES..... 60

1. Introduction.	60
2. Implementation of Committee Procedure in all EPA Programs Referencing 40 CFR Part 136.	60
3. EPA Leadership Role in Developing New Analytical Methods.	61
4. EPA Target Resources for Analytical Methods Where Most Needed.	61
5. Evaluate and Define Uses of Detection and Quantitation in Other Clean Water Act Programs.	61

CHAPTER 7 – IMPLEMENTATION.	63
1. Introduction.	63
2. Further Development of the Single Laboratory Procedure.	63
3. Additional Testing and Peer Review of the Single Laboratory Procedure.	64
4. Implementation of the New Regulations.	64

APPENDICES

Appendix A: Committee Charter

Appendix B: History of Committee’s Decisions

Appendix C: What we need a procedure to do

Appendix D: DQ FAC Single Laboratory Procedure v2.4

Appendix E: Uses Package (as distributed at the September 19-21, 2007 meeting)

Appendix F: Glossary of Terms

Appendix G: Contractor Information

Appendix H: References & Web Links

ACRONYMS

ACIL: American Council of Independent Laboratories
ASTM: American Society for Testing and Materials Standards
ASIWPCA: Association of State and Interstate Water Pollution Control Administrators
ATP: Alternative Test Procedures
CFR: Code of Federal Regulations
CWA: Clean Water Act
DL: Detection Limit
DL_{lab}: Laboratory Detection Limit
DL_{nat}: National Detection Limit
DL_{per}: Permit Detection Limit
DMR: Discharge Monitoring Report
DNQ: Detected but not Quantified
DQI: Data Quality Indicator
DQO: Data Quality Objective
ELG: Effluent Limitation Guideline
FACDQ: Federal Advisory Committee on Detection and Quantitation Approaches and Uses in Clean Water Act Programs
GLI: Great Lakes Initiative
ICIS: Integrated Compliance Information System
IDE: Interlaboratory Detection Estimate
IIAG: Inter-Industry Analytical Group
IQE: Interlaboratory Quantitation Estimate
ISO/IUPAC: International Organization for Standardization/International Union of Pure and Applied Chemistry
L_C: Critical value
LCMRL: Lowest Concentration Minimum Reporting Limit
L_D: Detection Limit
LTA: Long-Term Average
L_Q: Quantitation Limit
MCL: Maximum Contaminant Level
MDL: Method Detection Limit/ Minimum Detection Limit
ML: Minimum Level
MMA: Michigan Manufacturers Association
MQO: Measurement Quality Objective
MRL: Minimum Reporting Limit
NACWA: National Association of Clean Water Agencies
NELAC: National Environmental Laboratory Accreditation Conference
NPDES: National Pollutant Discharge Elimination System
OECA: US EPA's Office of Enforcement and Compliance Assurance
OGWDW: US EPA's Office of Ground Water and Drinking Water
OSW: US EPA's Office of Solid Waste
PCB: Polychlorinated biphenyl
POTWs: Publicly-Owned Treatment Works
PQL: Practical Quantitation Level
PT: Proficiency Testing
QL: Quantitation Limit
QL_{lab}: Laboratory Quantitation Limit

QL_{nat}: National Quantitation Limit
QL_{per}: Permit Quantitation Limit
QL_{state}: State Quantitation Limits
RDL: Reliable Detection Limit
RSD: Relative Standard Deviation
SOC: Synthetic Organic Chemicals
SVOC: Semivolatile Organic Compound
TMDL: Total Maximum Daily Load
USGS: United States Geological Survey
WET: Whole Effluent Toxicity
WQC: National Water Quality Criteria
WQS: State Water Quality Standards
WQBEL: Water Quality Based Effluent Limits

EXECUTIVE SUMMARY

Introduction

The US Environmental Protection Agency (EPA) is responsible for approving analytical procedures for monitoring pollutants in wastewater under the Clean Water Act. Detection (determining when a pollutant is present) and quantitation (determining the quantity of the pollutant) are significant issues for regulators, for the regulated community, for environmental laboratories that analyze wastewater for monitoring and compliance purposes, for other agencies that must use EPA-approved analytical methods, and for those who focus on human health and the environment.

By 2005, when EPA chartered the Federal Advisory Committee (Committee), concerns with the Method Detection Limit (MDL) procedure as published in 40 CFR 136 Part B were well characterized. The charge to the Committee was “to provide advice and recommendations on approaches for the development of detection and quantitation procedures and uses of these procedures in Clean Water Act programs.”

Over a 30-month period, the Committee worked diligently on challenging policy and technical issues related to detection and quantitation. The Final Report details all of the Committee’s recommendations.

Procedure for Detection and Quantitation

Early in its work, the Committee reached agreement on 15 statements that the Committee agreed accurately described “what we need a procedure to do.” These statements were subsequently used as criteria for evaluating potential procedures for detection and quantitation. The Committee selected five procedures to test in a pilot study. When reviewing the Pilot Study results, the Committee agreed that the ACIL procedure included most of the elements that members of the Committee had said they need a procedure to do. The Committee then revised the procedure based on the Pilot Study results to improve its performance, producing the ACIL-modified procedure.

When the Committee voted on the ACIL-modified procedure as the proposed single-laboratory procedure for determination of Detection Limits, the Committee did not reach consensus. However, the Committee did agree by consensus that EPA should implement an alternative procedure to the current detection and quantitation procedure cited at 40 CFR 136, Appendix B and noted that the ACIL-modified procedure contained elements that would be valuable to the agency in developing a new procedure.

Looking ahead to further work by EPA on procedure/s for detection and quantitation, the Committee recommended that a formal peer review of the procedure proposed for promulgation be undertaken and that a follow up pilot study be completed to confirm the performance of whatever procedure/s that EPA proposes to promulgate.

Data Quality

Data quality was never far from the Committee’s thoughts. The Committee approached this issue in two ways. First, the Committee reached agreement on Measurement Quality Objectives for purposes of pilot testing single laboratory detection procedures; however, the Committee was not able to reach agreement on Measurement Quality Objectives that would apply across the board.

The Committee’s second approach was to focus on the broader issue of Data Quality Objectives. In this area, the Committee reached consensus that EPA’s Office of Water should use the EPA Guidance on Systematic Planning Using the Data Quality Objectives Process in all Clean Water Act programs.

Uses of a Procedure for Detection and Quantitation

Initially, the Committee performed a preliminary review of most of the Clean Water Act programs and found potential differences in how these programs make use of method Detection and Quantitation Limits. Time did not permit the Committee to fully understand these differences so a decision was made early on to focus instead on the use of method Detection and Quantitation Limits in the National Pollutant Discharge and Elimination System (NPDES) program. As a result, the Committee affirmatively decided to table discussion and recommendations on uses of method detection and quantitation in other Clean Water Act programs.

The Committee did fully discuss and adopt recommendations for the determination and use of Detection and Quantitation Limits in NPDES permits and compliance processes, particularly in those situations where water quality based effluent limits (WQBELs) are less than Quantitation Limits. These situations present a challenge in setting permit limits and conditions as well as in making compliance determinations because of uncertainties surrounding the validity of the data. In these circumstances, the Committee fashioned a package of recommendations to be used by regulated parties, EPA and states in the areas of data reporting, calculation of monthly averages, and compliance determinations.

The Committee's recommendations on uses of Detection and Quantitation Limits in the NPDES process are dependent on a national benchmark for quantitation, the National Quantitation Limit. The concept of a National Quantitation Limit was a key component of a "package of uses recommendations" that the Committee developed over many months. It was also intended to define the minimum level of acceptable performance by a laboratory analyzing wastewater for compliance determinations.

In the end, the Committee did not reach consensus on the package of uses as a whole. Nonetheless, the Committee signaled its strong interest in further development of National Quantitation Limits in several important recommendations to EPA. First, the Committee recommended that EPA promulgate how the National Quantitation Limit will be derived and suggested a number of criteria that could be considered when EPA proposes such a procedure. Second, the Committee expressed a desire for EPA to promulgate new, more sensitive analytical methods while it develops the data necessary to support a National Quantitation Limit.

Additional Key Consensus Recommendations

Procedure Verification

- The Committee recommends that EPA give additional consideration to a higher frequency of Quantitation Limit verification and report its findings in the preamble of the *Federal Register* Notice and request specific comments on the final proposed frequency.
- The Committee recommends that during promulgation, EPA include and/or develop language to incorporate batch specific verification as an option in the detection and quantitation procedure.

Implementation of DQ FAC Single Laboratory Procedure v2.4 in all EPA Programs Referencing 40 CFR Part 136

- The Committee recommends that EPA programs that reference the present Part 136 Appendix B procedure consider adopting DQ FAC Single Laboratory Procedure v2.4 that would replace the current MDL procedure in Appendix B.

Implementation Tools

- The Committee recommends that EPA develop guidance and outreach materials for stakeholders as EPA implements the Committee's recommendations.
- The Committee recommends that EPA develop and implement guidance on the new procedures as well as a computer-based program to assist in calculating Detection and Quantitation Limits.

Measurement Quality Objectives

- The Committee recommends a $\leq 1\%$ false positive rate for detection.
- The Committee recommends that for promulgated methods listed in 40 CFR Part 136 without established Measurement Quality Objectives, the initial Measurement Quality Objective for quantitation (upon implementation of the new quantitation procedure) be a specific false negative rate ($\leq 5\%$) to be implemented through a multiplier of the Detection Limit, and that the precision and accuracy Measurement Quality Objectives for individual analytes/methods be generated and promulgated as the data to support those Measurement Quality Objectives becomes available.

Need for Assurance of Data Comparability

- The Committee recommends that, during the Data Quality Objectives process, EPA give special attention to assuring the analytical method produces comparable results, at or near the National Quantitation Limit, on split samples analyzed in different laboratories with the same method.

Promulgation of National Quantitation Limits for Existing and Future Methods

- The Committee recommends that National Quantitation Limits be promulgated in a Part 122 table by analyte.
- The Committee recommends that EPA generate National Quantitation Limits as rapidly as possible.
- The Committee recommends that National Quantitation Limits be promulgated only using the nationally promulgated approach.
- The Committee recommends that EPA may promulgate methods without promulgating a Quantitation Limit for that method. As new methods are proposed without a promulgated Quantitation Limit, data (e.g., Single Laboratory Detection, Single Laboratory Quantitation, etc.) showing demonstrated method performance should be included in the method. The methods should include a statement that these performance levels are guidance and may not always be achievable.

EPA Leadership Role in Developing Methods for Clean Water Act Programs

- The Committee recommends that EPA continue to act as the national lead for Clean Water Act programs in developing analytical methods and setting the performance standards for those methods.

Targeting Resources for Analytical Methods Where Most Needed

- The Committee recommends that EPA evaluate the federal resources dedicated to developing analytical methods with Detection/Quantitation Limits of sufficient quality that are capable of meeting the needs of Clean Water Act programs and adjust those resources, where necessary, to meet data quality and program needs.

Great Lakes Initiative Compliance

- The Committee recommends that its recommendations should not supersede the current Great Lakes Initiative provisions.

Conclusion

In conclusion, the Committee reached agreement on 15 statements which describe what a procedure should do in calculating Detection and Quantitation Limits. After testing five procedures in a pilot study and reviewing the results, the Committee could not reach consensus on a procedure for the determination of Detection and Quantitation Limits. However, the Committee did agree by consensus that EPA should implement an alternative procedure to the current detection and quantitation procedures cited at 40 CFR 136, Appendix B and that the ACIL-modified procedure contains elements that would be valuable to EPA in developing a new procedure.

The Committee developed a “package” of uses that represented a careful and delicate balance among the

various competing interests and positions of individual Committee members. The Committee expected that the package would be voted on, as a whole, in a single vote and members assumed that the entire package would be approved by consensus or the entire package would not be approved. Instead, five votes were taken on the “package” and some components of the package were approved by consensus while others were not.

The Committee made several important recommendations in regards to a National Quantitation Limit, Data Quality, Data Quality Objectives, and Measurement Quality Objectives. The Committee recommended that EPA promulgate how the National Quantitation Limit would be derived and suggested a number of criteria that could be considered when EPA proposes such a procedure. The Committee also recommended that EPA not delay promulgating new, more sensitive analytical methods while it creates the data necessary to support a National Quantitation Limit.

Additionally, the Committee reached agreement on other important issues related to detection and quantitation. These recommendations cover the areas of, procedure verification, guidelines and resource commitments on future analytical methods, implementation issues, and outreach.

TO THE READER

Committee Decision-making and Votes

The Committee's groundrules defined consensus as agreement of all members and consensus was the method of determining Committee agreement on issues. Members voted using one of three options: "agree," "disagree," or "not opposed." Consensus was defined as all members "agreeing" or "not opposed to" the decision. At Meetings #1 - #9, votes were tallied as totals for "agree," "disagree" or "not opposed." At Meeting #10 when final decisions were made on most recommendations, the Committee agreed to display their votes in the Final Report by caucus. Consequently, votes from Meetings #1 - #9 look different from votes at Meeting #10.

Where a proposed recommendation was approved by consensus, the result is referred to as a "recommendation" and is noted as "Approved By Consensus." Where a proposed recommendation was not approved, the result is referred to as a "decision" and the vote is noted as "Not Approved."

This report also references non-binding "straw polls" the Committee took during the deliberations to get a sense of Committee sentiment on proposed recommendations.

In Committee decision-making, EPA voted as the Office of Water.

Majority – Minority Reports for Non-Consensus Decisions

At Meeting 10 (September 19-21, 2007), the Committee agreed to provide majority and minority reports for non-consensus decisions. These reports follow the decision they relate to. Majority reports are followed by minority reports. The minority reports are indented to distinguish them from the majority reports.

Terms Used in the Report

A major focus of the Committee's work was to develop a recommendation on a procedure or procedures for Detection and Quantitation Limits to replace the procedures in 40 CFR, Part 136, Appendix B. Over the course of its 30 months of work, the Committee used several terms to describe a procedure which could be used by a single laboratory to determine its laboratory Detection and Quantitation Limits. The single laboratory procedure the Committee developed and voted on is consistently written as the "DQ FAC Single Laboratory Procedure v2.4."

As the Committee developed a package of recommendations on Uses, it proposed new concepts and terms to enable the package to be implemented. These terms (discussed in Chapters 3 and 4) include:

- National Quantitation Limit (referred to in many Committee documents as QL_{nat})
- Laboratory Detection Limit (referred to in many Committee documents as DL_{lab})
- Permit Quantitation Limit (referred to in many Committee documents as QL_{per})

During the deliberations of the Committee, the members adopted the convention of referring to analytical methods as "methods" and procedures for determining a Detection or Quantitation Limit as a "procedure." This report continues that convention.

Public Notice and Comment

The Committee recognized that EPA could not commit to promulgate the recommendations of the Committee without the benefit of public notice and comment. Wherever "promulgate" appears in the Final Report, the Committee's assumption is that EPA will propose a rule consistent with the Committee

recommendations and will fully consider public comments before deciding on its final actions.

CHAPTER 1 – PURPOSE OF THE COMMITTEE AND COMMITTEE PROCESS

1.1 Background

In 1999, several industry groups filed suit against EPA (*Alliance of Automobile Manufacturers, et al. v. EPA*, No. 99-1420, (D.C. Cir.) and in October, 2000, the parties reached a settlement agreement that required EPA to assess procedures to determine Detection and Quantitation Limits under EPA's Clean Water Act (CWA) programs by November 1, 2004. Pursuant to this agreement, on March 12, 2003, EPA issued for public comment a draft report assessing various detection and quantitation procedures and a proposed rule amending EPA's Method Detection Limit (MDL) and Minimum Level (ML) definitions and procedures. The vast majority of the 126 comments EPA received in response to the *Federal Register* notices were critical of the conclusion of EPA's assessment and proposed revisions.

1.2 Situation Assessment

Rather than proceeding with the revisions, EPA decided to withdraw the proposed rule and contract with a neutral third party, Triangle Associates, Inc., to conduct a situation assessment. The purposes of the situation assessment were to obtain additional input on technical and policy issues related to detection and quantitation and to explore the feasibility and design of a stakeholder process.

As a result of the interviews conducted for the situation assessment, Triangle Associates recommended that a Federal Advisory Committee be formed to address detection and quantitation issues and concluded that it had a good chance to achieve consensus on revised detection and quantitation approaches and uses in Clean Water Act programs. Triangle also found that many stakeholders interviewed believed that the process would only be successful with a strong commitment from EPA. To show this commitment, the Assessment Report recommended that EPA have a seat at the table."

1.3 Creation of the Committee

EPA accepted Triangle's recommendation and formed a Federal Advisory Committee under the Federal Advisory Committee Act on May, 2005. The two-year Charter for the Federal Advisory Committee on Detection and Quantitation Approaches and Uses in Clean Water Act Programs provided that the purpose of the Committee was to provide advice and recommendations on approaches for the development of detection and quantitation procedures and uses of these procedures in Clean Water Act programs. The Committee consisted of about 20 Committee members representing a diverse group of professionals from the following sectors: state government, environmental professionals, regulated industry, public utilities, and environmental community. (The Committee members, who were organized in caucuses, are listed on the report inner cover). The Committee charter was renewed on May 30, 2007 to give the Committee additional time to complete its work.

1.4 Committee Process

The Committee met 11 times; the first meeting was held on June 21-22, 2005 and the last meeting was held on December 5-6, 2007. A Technical Work Group was created at the outset of the Committee's work to carry out assignments on technical issues. The Technical Work Group, for example, was tasked with preparing papers on definitions relevant to detection and quantitation, presenting concepts, proposing criteria for evaluating possible detection and quantitation procedures, recommending procedures for the Pilot Study for the Committee's consideration, designing the Pilot Study, evaluating Pilot Study results, preparing a Pilot Study report, and many other tasks of a technical nature. Over the course of the Committee's work, the

Technical Work Group held 70 conference calls.

At the Committee's September 29-30, 2005 meeting, the Committee created a Policy Work Group. Its initial purpose was to 1) identify and define uses of detection and quantitation; 2) identify the existing situation for each use category and Data Quality Objectives for each type of use and user; and 3) pose policy issues that emerged in carrying out their assignments. The Policy Work Group was asked to identify issues, explore options, and draft documents to frame discussions of specific issues in advance of Committee meetings. The Committee would then take up the document at a Committee meeting for decision-making with the possibility of assigning subsequent tasks back to the work group that created it. The Policy Work Group held 42 conference calls and one face-to-face meeting.

The composition of both Work Groups reflected balanced membership from the Committee's caucuses.

As the Committee's work progressed, the Committee gave specific assignments to the Technical Work Group and to the Policy Work Group to carry out before the next Committee meeting.

More information and summaries of Committee meetings and meetings of the Technical Work Group and the Policy Work Group are available at www.epa.gov/waterscience/methods/det/index.html and in EPA's public docket, EPA-HQ-OW-2004-0041.

1.5 Definitions of Detection and Quantitation

In interviews conducted in the Situation Assessment that preceded the creation of the Committee, a number of parties had argued that EPA methods should adopt definitions of detection and quantitation that were consistent with or the same as those of the International Union of and Pure Applied Chemistry (IUPAC.) After the Committee convened, it ultimately decided against this approach because the IUPAC definitions could not be used as written since EPA methods allow: censored data, blanks not centered around zero, and non-constant standard deviation and generally disallow blank subtraction. While the Committee was in agreement with the IUPAC definition concepts, they were unable to adopt them as written, therefore the Committee agreed to include the IUPAC definitions in the glossary (Meeting #10, Decision 11.A).

The Committee agreed to the use of two points to define detection and quantitation for a number of reasons.

1. Two points are currently used by EPA (the MDL and ML) and these are conceptually equivalent to the Detection Limit and Quantitation Limit defined in the DQ FAC Single Laboratory Procedure v2.4
2. The Committee determined that while L_D could be defined in a simple way as 2 times L_C , (as it has been in the literature) such a predicted level was unlikely to be correct due to non constant variance, recovery that averages other than 100% and censoring in some methods. It would be extraordinarily difficult to confirm a predicted value for L_D , requiring hundreds of spikes at very closely spaced intervals.
3. Use of a three level system would be very difficult to implement. Laboratory reporting systems do not generally have the capability, and there is no definition of how the three levels would be utilized by the data user.
4. The Committee agreed that while the concept of the L_D was important it would be acceptable to not derive an L_D , as long as false negative error rate at the Detection Limit was acceptable for results at the Quantitation Limit (see Chapter 4, Section 4.2 item number 4 under "What we Need a Procedure to Do").
5. While the Committee definitions for Quantitation Limit do not specifically call out false negatives they do incorporate two important points which provide some protection against false negatives;
 1. The Quantitation Limit must be GREATER than the Detection Limit, this ensures that the False Negative error rate will be <50%.

2. That the appropriate Precision and Bias are achieved or demonstrated for the intended purpose.

The Committee then agreed to “working definitions” of detection and quantitation including two laypersons and two statistical definitions of detection, as follows:

DETECTION LIMIT (DL) – LAYPERSON'S DEFINITIONS

1. **Detection Limit (DL):** The minimum result which can be reliably discriminated from a blank (for example, with a 99% confidence level).
2. **Detection Limit (DL):** The lowest result that can be distinguished from the blank at a chosen level, α , of statistical confidence.

DETECTION LIMIT (DL) - STATISTICAL DEFINITIONS

1. **Detection Limit (DL):** Smallest measured amount or concentration of analyte in a sample that gives rise to a Type I error tolerance of α under the null hypothesis that the true amount or concentration of analyte in the sample is equal to that of a blank. (The alternative hypothesis is that the true amount or concentration of analyte is greater than that of a blank.)
2. **Detection Limit (DL):** The minimum observed result such that the lower 100 $(1 - \alpha)$ % confidence limit on the result is greater than the mean of the method blanks.

Vote: 12 Agree, 7 Not Opposed, 0 Disagree, 1 Absent
Approved By Consensus

States: 4 Agree,
Labs: 2 Agree, 2 Not Opposed
Industry: 4 Agree
EPA: 1 Not Opposed
Public Utilities: 4 Not Opposed
Environmental Community: 2 Agree, 1 Absent
Meeting #10, Decision 11.B

QUANTITATION LIMIT (QL) - DEFINITIONS

1. **Quantitation Limit (QL):** The smallest detectable concentration of analyte greater than the Detection Limit (DL) where the accuracy (precision & bias) achieves the objectives of the intended purpose.
2. **Lab Quantitation Limit (QL_{lab}):** The smallest detectable concentration of analyte greater than the Detection Limit (DL) where the accuracy (precision & bias) demonstrated by the laboratory achieves the objectives of the intended purpose.

Vote: 3 Agree, 16 Not Opposed, 0 Disagree, 1 Absent
Approved By Consensus

States: 4 Not Opposed,
Labs: 4 Not Opposed
Industry: 1 Agree, 3 Not Opposed
Public Utilities: 4 Not Opposed
EPA: 1 Agree
Environmental Community: 1 Agree, 1 Not Opposed, 1 Absent
Meeting #10, Decision 11.B

CHAPTER 2 – DATA QUALITY OBJECTIVES AND MEASUREMENT QUALITY OBJECTIVES

2.1 Introduction

The Committee recognized the importance of following a Data Quality Objectives process in developing performance and acceptance criteria for data to be used in detection and quantitation decisions. This process includes identification of appropriate Data Quality Indicators, defined as quantitative and qualitative measures of data quality attributes such as precision, accuracy, and representativeness. This process also includes establishment of Data Quality Objectives, or qualitative and/or quantitative statements which, in the context of detection and quantitation decisions, define the appropriate type of data needed to achieve the required decision certainty. Finally, the process involves the selection of Measurement Quality Objectives, or specific quantitative measures of performance in relation to particular Data Quality Indicators, such as specific values for precision, bias, and false positive or false negative error rates.¹

The Committee recognized that EPA has developed, through its Quality System program, a number of guidance documents related to environmental data quality, in particular in relation to a project-specific Data Quality Objectives process.² However, there has been less focus on applicability to more routine monitoring done as part of mandatory programs (e.g., National Pollutant Discharge Elimination System or NPDES compliance monitoring under the Clean Water Act.) The Committee attempted to address Data Quality Objective and Measurement Quality Objective issues in the context of decision certainty in NPDES compliance specifically as they related to detection and quantitation.

This chapter discusses the Committee's recommendations on some of these issues. Although the specifics of applying the Data Quality Objectives process to other aspects of the Clean Water Act program were not discussed, this chapter presents discussions and recommendations regarding the application of the same principles and practices that were discussed in the context of NPDES compliance testing to other aspects of the program. The chapter continues with more detailed discussion and recommendations with an emphasis on Data Quality Objectives and Measurement Quality Objectives appropriate for NPDES permit compliance testing.

All detection and quantitation procedures considered by the Committee require the selection of one or more Measurement Quality Objectives (e.g., false positive rate, false negative rate, accuracy, and/or precision). In some instances, procedures were designed around a particular Measurement Quality Objective. For example,

1 More specific or detailed definitions of these key terms in the Data Quality Objectives Process utilized by EPA include the following:

Data Quality Indicators: quantitative and qualitative measures of principal quality attributes, such as precision, accuracy, representativeness, and sensitivity.

Data Quality Objectives: qualitative and quantitative statements that clarify study objectives, define the appropriate type of data, and specify tolerable levels of potential decision errors that will be used as the basis for establishing the quality and quantity of data needed to support decisions.

Measurement Quality Objectives: "acceptance criteria" for the quality attributes measured by project data quality indicators. During project planning, measurement quality objectives are established as quantitative measures of performance against selected data quality indicators, such as precision, bias, representativeness, completeness, comparability, and sensitivity.

Source: US EPA, Guidance on Environmental Data Verification and Data Validation (QA/G-8), EPA/240/R-02/004, November 2002, <http://www.epa.gov/quality/qs-docs/g8-final.pdf>.

²See, for example, US EPA, *Guidance on Systematic Planning Using the Data Quality Objectives Process (QA/G-4)*, EPA/240/B-06/001, February 2006, <http://www.epa.gov/quality/qs-docs/g4-final.pdf>, and other documents available at <http://www.epa.gov/quality/>.

all procedures considered by the Committee for detection target a 1% false positive rate. In discussion, it was generally agreed that detection would not require specific accuracy or precision. As evidenced by the definition of quantitation adopted by the Committee (*refer to page 2*), it was agreed that at least accuracy and precision would be required for determining quantitation and that the Quantitation Limit must be greater than the Detection Limit.

Because the detection and quantitation procedures require that these Measurement Quality Objectives be addressed, it was appropriate for the Committee to discuss how Measurement Quality Objectives would be set or determined. Initial discussion on specific numerical values for many potential Measurement Quality Objectives failed to result in indications that Committee consensus could be achieved. Thus, the Committee decided to consider broader or more general recommendations rather than continue to try to achieve consensus on specific numerical values. This approach led to the following proposed recommendations and decisions.

2.2 Recommendations and Decisions on Data Quality Objectives

The Committee recognized that the charter directed the Committee to consider recommendations with respect to determination and use of detection and quantitation in the Clean Water Act. The Committee considered and discussed the application of the Data Quality Objectives setting process as an appropriate process for determining what Measurement Quality Objectives and Data Quality Indicators would be suitable for different uses within the Clean Water Act program. The Committee determined that it would be appropriate to apply such a process (although it did not discuss the process in detail) to all components of the Clean Water Act program and made the following recommendation accordingly.

Data Quality Objective Recommendation

The Committee recommends that the EPA Office of Water use the *EPA Guidance on Systematic Planning Using the Data Quality Objectives Process* in all Clean Water Act programs.

Vote: 17 Agree, 0 Not Opposed, 0 Disagree, 1 Absent

Approved By Consensus

Meeting #7, Decision 3

In the Committee's discussion of this recommendation it was made clear that the intent was not to require that the Office of Water follow the referenced document strictly or in all detail. Rather, the intent was to indicate that EPA should go through a Data Quality Objectives process that looks at decision uncertainty (e.g., the compliance decision), determine what Measurement Quality Objectives are appropriate, and derive Measurement Quality Objectives consistent with the decision uncertainty requirements. It was made equally clear that the Office of Water's current approach of picking a measurement technology and then targeting Measurement Quality Objectives consistent with that technology's historical performance was not an appropriate Data Quality Objectives process.

Establishing Data Quality Objectives for Decision-Making in Clean Water Act Programs

The Data Quality Objectives process is intended to assure appropriate decision-making certainty and, thus, is equally applicable throughout all aspects of the Clean Water Act program. Time did not permit detailed Committee discussions or recommendations but that does not imply application of a Data Quality Objectives process is not equally important in other aspects of the program. This recommendation expands on the previous recommendation and begins to provide more detail and clarity to the intent of the Committee. Therefore, the Committee considered the broader issue and voted on the following recommendation.

The Committee recommends that EPA establish Data Quality Objectives (with indicators and Measurement Quality Objectives) for Clean Water Act programs where Detection/Quantitation Limits are used in decision making.

Vote: 15 Agree, 4 Not Opposed, 1 Disagree
Not Approved

States: 3 Agree, 1 Not Opposed

Labs: 1 Agree, 3 Not Opposed

Industry: 4 Agree

Public Utilities: 4 Agree

EPA: 1 Disagree

Environmental Community: 3 Agree

Meeting #10, Decision 5.G

Majority Report

This recommendation was developed to provide clarity to the intent of the Committee regarding the Data Quality Objectives process recommended by the Committee. EPA's Data Quality Objective guidance states that specific Data Quality Objectives, Data Quality Indicators and Measurement Quality Objectives should be adopted prior to beginning any study or data collection effort. Data Quality Indicators may include measures of data quality including, but not limited to, accuracy, precision, false positive and negative rates, comparability, representativeness and completeness. For example, EPA should consider adopting a Measurement Quality Objective for accuracy at the Quantitation Limit to define the quality of data at that limit, thereby determining actions that can be taken given the quality of that data. Data Quality Indicators are accompanied by corresponding Measurement Quality Objectives defining the limits of acceptability for each Data Quality Indicator.

The Committee did not reach consensus on which Data Quality Indicators and corresponding Measurement Quality Objectives should be recommended other than for the false positive rate at the detection level. However, the majority of the Committee does believe that EPA should evaluate the uses of data in all Clean Water Act programs and determine the quality of data required to meet those uses prior to making regulatory decisions where detection and quantitation are in question.

The Industry and Public Utility caucuses believe Measurement Quality Objectives may not be achievable by the performance of current analytical methods and that, when Measurement Quality Objectives are not achievable, the use of data generated using these methods must also be limited, in contrast to methods and data with acceptable uncertainty.

The intent of the majority of the Committee in this recommendation is not to allow analytical methods alone to define the Measurement Quality Objectives for Clean Water Act programs but to consider method performance when adopting Measurement Quality Objectives and to modify the use accordingly, when necessary. For example, the Measurement Quality Objective for accuracy at the Quantitation Limit when determining compliance with a permit limit may be more rigorous than a method can provide. The industry and public utility caucuses believe this situation would require modification of the use (compliance determinations, in this example) unless a method could be identified or developed that meets the Measurement Quality Objective for the use.

Minority Report

The EPA voted to disagree with the recommendation "Establishing Data Quality Objective's for Decision-making in Clean Water Act Programs" based on concerns about resources. The core

recommendations of the Committee – pilot test the new single laboratory procedure, promulgate and implement new rules incorporating the single laboratory procedure, propose an algorithm for determining the National Quantitation Limit, and define the uses of detection and quantitation in compliance and enforcement of NPDES permits – will require significant EPA resources over the next several years. At this time, EPA cannot commit additional resources to several of the other recommendations of this report, including the recommendation, “Establishing Data Quality Objective’s for Decision-making in Clean Water Act Programs,” until these core recommendations are implemented.

2.3 Recommendations and Decisions on Measurement Quality Objectives for Measurements Used in NPDES Compliance Testing

The Committee’s discussions with respect to Measurement Quality Objectives focused on NPDES permitting and compliance testing.

Measurement Quality Objective for Detection – False Positive Rate

The Committee recommends that a $\leq 1\%$ False Positive rate be used for Detection.

Vote: 17 Agree, 0 Not Opposed, 0 Disagree, 1 Absent
Approved By Consensus

Meeting #7, Decision 4.A

There was consensus with the general premise that detection should target a false positive rate of $\leq 1\%$. This is consistent with most historical and international definitions of detection. Furthermore, all Detection Limit procedures considered in the Pilot Study were designed to implement this Measurement Quality Objective. The IUPAC definitions for detection (L_D) included control of false negatives ($\leq 5\%$). The Committee agreed to ignore false negatives for detection only if they were incorporated in the concept of quantitation.

Measurement Quality Objectives for Quantitation for Promulgated Methods

The Committee recommends that for promulgated methods in 40 CFR Part 136 without established Measurement Quality Objectives, the initial Measurement Quality Objectives for quantitation upon implementation of the new quantitation procedure is a specific false negative rate ($\leq 5\%$) to be implemented through a multiplier of the Detection Limit (determined by the DQ FAC Single Laboratory Procedure v2.4). The precision and accuracy Measurement Quality Objectives for individual analytes/methods would be generated and promulgated, as the data to support those Measurement Quality Objectives becomes available.

Vote: 17 Agree, 0 Not Opposed, 0 Disagree, 1 Absent
Approved By Consensus

Meeting #7, Decision 4.C

Throughout discussions of setting Measurement Quality Objectives the problem of how any Measurement Quality Objective would apply retroactively to methods currently promulgated at 40 CFR Part 136 came up. A primary concern was that some of the existing promulgated methods may not fully meet the universally established Measurement Quality Objectives and could be questioned on their appropriate use for regulatory compliance. The recommendation attempted to outline a process that could be applied to existing Part 136 methods that would essentially characterize their performance and use that performance as the basis for establishing Measurement Quality Objectives that would be written into the analytical methods. Although the

Technical Work Group was charged with coming up with a procedure for turning the data that would be collected into Measurement Quality Objectives for the methods, time limitations prevented it from developing the requested procedure.

Decisions on Measurement Quality Objectives for Future Promulgation of Methods

Straw polls indicated that the Committee could not come to consensus on setting fixed Measurement Quality Objectives for quantitation in the context of NPDES permit compliance testing. A proposal was put forth as a compromise that might be more acceptable to the majority of the Committee. There were several key components to this proposal. First, the scope was limited to future promulgation of methods in Part 136 thus setting aside the difficulties of applying any Measurement Quality Objectives to existing methods. The second aspect was that the Measurement Quality Objective would be targets but EPA could still promulgate the target if those Measurement Quality Objectives were not achieved. However, EPA would be required to provide a rationale why they felt the needs of the Clean Water Act program justified promulgating a method that failed to meet the target. The final aspect of the proposal was that there would be some bounds on the Measurement Quality Objectives where it would not be considered acceptable to promulgate the method in Part 136. This proposal was discussed and voted on in the following two decisions.

The Committee recommends, for future method promulgation, that target Measurement Quality Objectives for Data Quality Indicators, such as precision, accuracy, Method Specified Qualitative Identification, and false negative error rates derived from the Data Quality Objectives process, be established for Quantitation Limits in Part 136. If the target Measurement Quality Objectives cannot be met, EPA may promulgate with rationale.

Vote: 16 Agree, 2 Not Opposed, 1 Disagree
Not Approved

Meeting #3, Decision 2

Majority Report

This recommendation was a compromise to having a fixed set of Measurement Quality Objectives for NPDES permit compliance testing. It is entirely consistent with the consensus recommendation that EPA should use the decision uncertainty Data Quality Objectives process to establish Measurement Quality Objective goals (not limits). It allows flexibility for the Data Quality Objectives process to determine which Measurement Quality Objectives need to be set and which Data Quality Indicators are appropriate for a specific situation. Furthermore, it does not require EPA to set a single set of Measurement Quality Objectives. EPA could implement the recommendation in a general sense or by allowing issues specific to the substance to be taken into account. The proposed recommendation also acknowledges that there may be some circumstances where, despite EPA's best efforts, it may not be able to achieve the Measurement Quality Objective goals. In these circumstances, the recommendation requires EPA to provide a rationale that may include how it attempted to achieve the goals, what performance it was able to obtain, and why the unique circumstances of the substance and/or threat to human health or the environment may warrant accepting analytical method performance less than the Measurement Quality Objective goals. The essence of the recommendation is use of the decision uncertainty Data Quality Objectives process to establish Measurement Quality Objective goals and transparency when those goals cannot be achieved. The recommendation was crafted to afford EPA as much flexibility as possible.

Minority Report

EPA disagrees with the recommendation that "... target Measurement Quality Objectives established for Quantitation Limits. If the target Measurement Quality Objectives cannot be met, EPA may promulgate with rationale." EPA also disagrees with the recommendation that "a single set of Measurement Quality Objective bounds be established for promulgated Part 136 methods that define Quantitation for Clean Water Act compliance and enforcement uses."

These recommendations would establish Measurement Quality Objectives for analytical methods that might be used in a variety of environmental decision-making situations without regard to what decision error might be acceptable. EPA believes that this runs counter to the Data Quality Objectives process currently used by EPA which considers the intended use of an analytical result and examines the extent and nature of the uncertainty that should be allowed. In addition, under the "bounds" recommendation, EPA would have the burden to provide a rationale for a method's performance without knowing what type of environmental decision would be made with the analytical results. Despite this, EPA does agree that, in making enforcement and compliance determination, the uncertainty in the data should be taken into account.

Target Measurement Quality Objective Bounds Decision

The Committee recommends that a single set of Measurement Quality Objective bounds be established for promulgated Part 136 methods that define Quantitation for Clean Water Act compliance and enforcement uses.

Vote: 7 Agree, 3 Not Opposed, 8 Disagree, 2 Absent

Not Approved

States: 3 Not Opposed, 1 Disagree

Labs: 3 Disagree, 1 Absent

Industry: 3 Agree, 1 Absent

Public Utilities: 4 Agree

EPA: 1 Disagree

Environmental Community: 3 Disagree

Meeting #10, Decision 7

Majority Report

The need for Measurement Quality Objective bounds and this recommendation grew from a compromise a majority of Committee members supported that stated that EPA should use the Data Quality Objectives process to set Measurement Quality Objective targets (as opposed to limits) for appropriate Measurement Quality Objectives for NPDES permitting. If circumstances were such that EPA could not achieve those Measurement Quality Objective targets, it would be acceptable for it to propose the method anyway, provided that it provided a rationale explaining the compelling need to use a method that failed to meet target Measurement Quality Objectives. However, the subject recommendation suggests, that for NPDES compliance testing, there should be some level of performance below which one could simply not consider the data quantitative and suitable for determining compliance. A majority of Committee members agreed or didn't oppose that quantitation bounds should be established in the context of providing a floor and ceiling for Measurement Quality Objectives derived during the Data Quality Objectives process addressing NPDES permit compliance testing. Based on the Committee consensus definition of "Quantitation Limit," detection is stated as one such bound (Quantitation Limit > Detection Limit).

Qualitative identification criteria are also required by several Part 136 methods as a threshold to determine the presence of a specific analyte. A result that meets qualitative identification criteria is expected to pass a higher bar than detection. At quantitation the result must not only be detectable, but the false negative error

rate and accuracy (precision and bias) must be acceptable for the intended use of the data. It is also important that a quantifiable result be repeatable and verifiable in order to base regulatory decisions upon it. A majority of Committee members agreed or were not opposed to clear bounds for quantitation established by EPA for compliance and enforcement. The Committee definition of quantitation is based on the level at which accuracy and precision for the intended purpose are achievable. Presumably these would be criteria determined as target Measurement Quality Objectives during the Data Quality Objectives process.

Minority Report

EPA and others disagreed with the recommendation that “a single set of Measurement Quality Objective bounds be established for promulgated Part 136 methods that define Quantitation for Clean Water Act compliance and enforcement uses.” EPA disagrees with this version of the “bounds” recommendation because it would establish a Measurement Quality Objective floor (bound), below which no methods would be allowed to perform without even the off ramp of a rationale. EPA believes that this runs counter to the Data Quality Objectives process currently used by EPA which considers the intended use of an analytical result and examines the extent and nature of the uncertainty that should be allowed. Despite this, EPA does agree that in making enforcement and compliance determination, the uncertainty in the data should be taken into account.

One member of the Laboratory Caucus opposes the establishment of target Measurement Quality Objective bounds under the Clean Water Act because of the “universal” nature of the proposal. The spectrum of data use under the Clean Water Act is so broad that establishing universal bounds would lead to an abundance of instances where the “bounds” would be too broad or not stringent enough for the intended use of the data. This would lead to data being used that are not of sufficient quality to support its use or the unnecessary rejection of data that does support its intended use. The concept of having “bounds” for objectives also seems to be somewhat of an oxymoron. This member does agree that an assessment of data quality and the Data Quality Objectives process is essential for proper decision-making under the Clean Water Act.

2.4 Measurement Quality Objectives for Clean Water Act Uses

The Committee also considered Measurement Quality Objectives in the broader context Clean Water Act uses that may go beyond NPDES permitting. In those discussions, the Committee considered a recommendation that would set outer bounds for Measurement Quality Objectives but could not come to consensus on the specifics. The Committee then considered the following recommendation which, if implemented, would have EPA consider appropriate bounds further and then publish the Measurement Quality Objective bounds that it determines are appropriate for public comment.

Measurement Quality Objective Bounds

The Committee recommends that EPA establish quantitative Measurement Quality Objective bounds for relevant Data Quality Indicators that define Quantitation for intended Clean Water Act uses. These bounds would be offered for public comment by EPA.

Vote: 9 Agree, 7 Not Opposed, 1 Disagree, 1 Absent
Not Approved

Meeting #7, Decision 4.E

Majority Report

A majority of Committee members agreed with or were not opposed to the general concept that there should be some outside boundary for Measurement Quality Objectives or Data Quality Indicators beyond which a method may not be suitable for a particular purpose. However, the Committee did not agree on specific values for Measurement Quality Objective bounds or even that universal bounds for all different Clean Water Act uses were appropriate.

However, just because the Committee could not resolve these questions within the time available does not imply that the Committee did not think these questions were not worth addressing. The recommendation was intended to convey that sentiment and to encourage EPA to continue to try to find an acceptable process for establishing Measurement Quality Objective bounds for Clean Water Act purposes. The recommendation does not imply any constraints on how this might best be accomplished and it does not imply any universal, fixed Measurement Quality Objective bounds. Because of the issues raised by Committee members during the discussions, the recommendation goes on to indicate that EPA should present, for public comment, the results of its final determinations with regard to the question of Measurement Quality Objective bounds for Clean Water Act.

Minority Report

EPA disagrees with the recommendation that “a single set of Measurement Quality Objective bounds be established for promulgated Part 136 methods that define Quantitation for Clean Water Act compliance and enforcement uses.”

These recommendations would establish Measurement Quality Objectives for analytical methods that might be used in a variety of environmental decision-making situations without regard to what decision error might be acceptable. EPA believes that this runs counter to the Data Quality Objectives process currently used by EPA which considers the intended use of an analytical result and examines the extent and nature of the uncertainty that should be allowed. In addition, under the “bounds” recommendation, EPA would have the burden to provide a rationale for a method’s performance without knowing what type of environmental decision would be made with the analytical results. Despite this, EPA does agree that in making enforcement and compliance determination, the uncertainty in the data should be taken into account.

CHAPTER 3 – PROCEDURES FOR DETECTION AND QUANTITATION

3.1 Introduction

The principal charge to the Committee was to develop recommendations on approaches for determining Detection Limits, Quantitation Limits, and their uses in Clean Water Act programs. After two and one-half years of activities by several work groups involving deliberations, design and assessment of a Pilot Study, and production of numerous working documents, Committee members had developed a clear understanding of the complexity of the scientific, science-policy, and policy issues involved with low-level analytical measurements in support of Clean Water Act programs. A central challenge confronting the Committee (and thus EPA) was in developing the framework for a program involving detection and quantitation that is both technically/statistically rigorous while being able to be practically implemented by regulatory agencies, regulated entities and laboratories, all within the broad purview of the Clean Water Act.

The Committee discussed three basic types of procedures for determining Detection and Quantitation Limits. Although a formal definition was never adopted, the Committee had extensive discussion regarding what was termed a single laboratory procedure. This is a procedure which is performed by a laboratory to determine the laboratory specific Detection and Quantification Limits. The second type of procedure the Committee discussed was an inter-laboratory procedure. The Committee did adopt a definition for what constitutes an inter-laboratory procedure¹ but, in simple terms, such a procedure involves distributing identical samples to multiple laboratories for analysis and then using the resulting data to calculate a single Detection and/or Quantitation Limit representative of the participating laboratories. The final type of procedure discussed was a multi-laboratory procedure. The Committee also adopted a definition for what constitutes a multi-laboratory procedure² but, in simple terms, such a procedure involves pooling of single laboratory estimates of detection and/or quantitation to calculate a multi-laboratory estimate of the detection and/or quantitation capabilities of the laboratories.

During the deliberations of the Committee, the members adopted the convention of referring to analytical methods as “methods” and procedures for determining a Detection or Quantitation Limit as “procedures.” This report continues that convention.

3.2 What The Committee Needs A Procedure To Do

Over the course of multiple Committee meetings, the Committee developed and agreed to the document, “What we need a procedure to do.” (See Appendix B.) This document contains 15 objectives, initially developed for use in the Pilot Study, to evaluate how well the procedures tested met the objectives.

¹ The definition of an inter-laboratory procedure adopted by the Committee is as follows: A study where a centralized study design coordinator sends identical samples to multiple different laboratories for analysis. The resulting raw data are analyzed by the study design coordinator by a given procedure to provide estimates of L_C , L_D and/or L_Q . The laboratories would generate only data that would be submitted to the study design coordinator who would compile the data, evaluate it and generate an inter-laboratory L_C , L_D and/or L_Q .

² The definition of multi-laboratory procedure adopted by the Committee is as follows: A study where multiple laboratories individually perform a L_C , L_D and/or L_Q estimation procedure (usually using self selected spiking concentrations) and those individual estimates are summarized in some fashion (e.g. averaging, upper or lower confidence intervals) to characterize some measure of how well the analytical method performs in qualified laboratories. The multi-lab procedure study would include two steps; First, each individual lab would conduct the analysis and generate its unique L_C , L_D and/or L_Q level. Second, those levels would then be compiled from all laboratories, evaluated, and based on criteria, used to propose multi-lab L_C , L_D and/or L_Q levels, where appropriate.

Committee members also generally agreed that the pilot test was an opportunity to inform the Committee's final recommendations and that some of the objectives might be refined as a result of the Pilot Study data.

The 15 objectives of the document "What we need a procedure to do" follow. The term "limit" is used generally to refer to Detection and Quantitation Limits since the Committee had not yet defined them:

1. Does the procedure provide an explicit estimate of bias at L_Q for limits that must be verifiable by labs at those limits?
2. Does the procedure provide an explicit estimate of precision at L_Q for limits that must be verifiable by labs at those limits?
3. Does the procedure provide an explicit false positive rate for L_C ?
4. Does the procedure provide an explicit false negative rate at L_C for the true value at L_D or L_Q that must be observed in labs at L_C for the estimated values of L_D or L_Q ?
5. Does the procedure provide that qualitative identification criteria defined in the analytical method are met at the determined Detection and Quantitation Limits?
6. Does the procedure adequately represent routine variability in laboratory performance?
7. Does the procedure perform on-going verification of estimates?
8. Is the procedure capable of calculating limits using matrices other than laboratory reagent grade water?
9. Does the procedure use only data that results from test methods conducted in their entirety?
10. Does the procedure explicitly adjust or account for situations where method blanks always return a non-zero result/response?
11. Does the procedure explicitly adjust or account for situations where method blanks are intermittently contaminated?
12. Is the procedure clearly written with enough detail so most users can understand and implement it?
13. Is the procedure cost-effective?
14. Does the procedure assess multi- and inter-laboratory variability when data from more than one laboratory is used?
15. Is the procedure applicable to all users and test methods?

As part of the decision-making process, the procedures tested in the Pilot Study were subsequently evaluated according to how well they met the 15 objectives.

3. Additional Requirements Based on Contemplated Uses of Detection and Quantitation in the Clean Water Act Program

As the discussion of uses of detection and quantitation in Clean Water Act programs developed, other potential requirements for the single laboratory procedure became apparent. During the deliberations the requirements were not clear but when the final Clean Water Act detection and quantitation use recommendations were identified, there were two requirements that the single laboratory procedure needed to meet.

One was a need to determine the lowest possible concentration that a laboratory could detect a substance. This was important because this was discussed as a threshold below which permittees would be required to report not-detected and above which permittees would either report detected but not quantified or the numeric value if the result was above the Permit Quantitation Limit.

The other was the capability to demonstrate that a Laboratory Quantitation Limit was below the Permit Quantitation Limit. This aspect of the procedure would be utilized to determine if the laboratory's capabilities were sufficient to meet the NPDES permit compliance testing requirements.

Additional details of how these requirements fit into the overall NPDES permitting strategy developed by the Committee can be found in Chapter 3.

3.4 Pilot Study Design

The process proposed for the Committee's work included pilot testing any procedure/s recommended by the Committee to confirm that the procedure performed as expected before the Committee finalized its recommendation on one or more procedures. However, a number of Committee members expressed concern over how they could decide among the candidate procedures without data on performance. It was therefore decided to pilot test several candidate procedures to help inform the Committee's decision-making process. Thus, the Committee undertook to select procedures to pilot test, developed a study design for the pilot test and, to the extent possible within strict budget and time constraints to, verify the performance of candidate detection and quantitation procedures.

3.5 Pilot Study

According to the analyte list provided in the Pilot Study Report, a total of 104 analytes were included in the study and, of that dataset, 55 were evaluated during the assessment portion of the study.

The Committee affirmatively agreed to pilot test the following EPA approved methods:

- 200.7 (Determination of Metals and Elements in Waters and Wastes by Inductively Coupled Plasma-Atomic Emission Spectroscopy),
- 300.0 (Determination of Inorganic Ions by Ion Chromatography - Method A),
- 625 (Base Neutrals and Acids by GC/MS),
- 08 (Organochlorine Pesticides and PCBs by GC/ECD) and,
- 335.4 (Total Cyanide by Semi-automated Colorimetry).

These methods were selected to represent a cross section of measurement technologies that appear in 40 CFR Part 136 and to provide a good test of the performance of the procedures.

To begin the process of recommending procedure/s for determining Detection and Quantitation Limits of an analytical procedure, the Committee charged the Technical Work Group to compile a list of candidate procedures. The Technical Work Group used the framework provided by the document, "What we need a procedure to do," to select procedures for further consideration. The resulting list of procedures is shown in Table 1. This list of procedures included single laboratory procedures, inter-laboratory procedures, and procedures that, although written as single laboratory or inter-laboratory, could be easily modified and implemented as either single laboratory or inter-laboratory procedures. No multi-laboratory procedures were proposed. After reviewing the initial list, the Committee asked the Technical Work Group to narrow the list. The Technical Work Group accomplished this task by identifying candidate procedures that were more conceptual in nature and thus lacked a specific written procedure to implement them. These procedures, shown at the bottom of Table 1, were dropped from consideration.

Table 1 Summary of Detection and Quantitation Procedures Considered by the Committee

Procedures	Detection	Quantitation	Pilot Tested
American Council of Independent Laboratories (ACIL) Proposed Procedures for Determining the Method Detection Limit and Quantitation Limit	X	X	X
Proposed Procedures for Estimating the Limit of Detection, Consensus Group Committee I on Detection for Proposal to USEPA for Replacement of 40 CFR, Part 136 Appendix B MDL Procedure	X	X	
Determination of Detection Limits Using Laboratory QC, East Bay Municipal Utilities District	X		
Hubaux-Vos Detection Limit Procedure	X		X ¹
ASTM Interlaboratory Detection Estimate (IDE)	X		X ⁵
EPA MDL, 40 CFR Part 136, Appendix B	X		
ASTM Interlaboratory Quantitation Estimate (IQE)		X	X ⁵
EPA OGWDW Lowest Concentration-Minimum Reporting Level (LC-MRL) for Quantitation		X	X ⁵
EPA Minimum Level		X	
Procedures Dropped from Consideration			

¹ Procedures were pilot tested as both single laboratory and inter-laboratory procedures.

Water Research Centre Determination and Quantitation	X		
ISO/IUPAC	X	X	
IIAG Sensitivity Test & Full - Range Validation Study	X		
Office of Solid Waste (OSW) Quantitation Limit		X	
NELAC Uncertainty Calculations			
USGS LT-MDL			

The Committee decided to require the same Measurement Quality Objective targets for every chemical and analytical method studied, as most of the procedures allowed for some flexibility in selection of different Measurement Quality Objectives. These tests, performed over several weeks, used blanks and spiked samples that may have encompassed several different concentrations of the target analyte. The Measurement Quality Objectives recommended by the Technical Work Group and approved by the Committee for the Pilot Study were 20% RSD, 50% to 150% mean recovery range, and false positive and false negative rates of $\leq 1\%$.

There was considerable discussion over whether to pilot test the American Council of Independent Laboratories (ACIL) Proposed Procedures for Determining the Method Detection Limit and Quantitation Limit or the Proposed Procedures for Estimating the Limit of Detection, Consensus Group Committee I on Detection for Proposal to USEPA for Replacement of 40 CFR, Part 136 Appendix B MDL Procedure (Consensus Group Procedure.) The procedures are very similar in many respects. The decision was made to modify the ACIL procedure by specifying the use of K instead of Student t for censored methods, thereby making it more like the Consensus Group Procedure Committee I on Detection for Proposal to USEPA for Replacement of 40 CFR, Part 136 Appendix B MDL Procedure. The ACIL procedure was further modified by changing some of the specified Measurement Quality Objectives in the procedure to match those selected for the Pilot Study. The $\leq 1\%$ false positive criterion was already implemented in the original procedure. The recovery criterion was changed to a mean of 50-150%; the standard deviation of spikes at the Quantitation Limit had to be $< 20\%$ and the Quantitation Limit had to be at least a factor of two times the Detection Limit. These changes were implemented in Revision 5 of the ACIL procedure.

The Technical Work Group recommended and the Committee approved pilot testing of the five procedures noted in the last column of Table 2.1:

- American Council of Independent Laboratories (ACIL) Proposed Procedures for Determining the Method Detection Limit and Quantitation Limit, Revision 5
- Hubaux-Vos Detection Limit Procedure
- ASTM Interlaboratory Detection Estimate (IDE)
- ASTM Interlaboratory Quantitation Estimate (IQE)
- EPA OGWDW Lowest Concentration-Minimum Reporting Level (LC-MRL) for Quantitation

3.6 Committee Decision-Making Process On A Single Laboratory Detection and Quantitation Procedures

At the completion of the Pilot Study, the Committee determined that the ACIL single laboratory procedure performed as well as or better than the other procedures and met most of the “What we want a procedure to do” characteristics. The Committee directed the Technical Work Group to work on modifying the ACIL procedure as indicated by the Pilot Study results and informed by concepts from the Consensus Group procedure and Laboratory QC procedure for single laboratory uses. A sub-group of the Technical Work Group worked on implementing that charge, resulting in drafting of DQ FAC Single Laboratory Procedure v2.4, which was then considered by the Committee.

At the September 19-21, 2007 meeting, a straw poll of the Committee regarding a recommendation that EPA adopt the DQ FAC Single Laboratory Procedure v 2.4 indicated that several Committee members had issues they needed to resolve before they could support the recommendation. These included issues related to several questions about verification frequency (both with respect to the frequency of blank or spike sample analyses as well as the frequency that the Detection or Quantitation Limits are evaluated with respect to the blank or sample analyses), a change from mandatory to optional re-calculations and a desire to have a batch specific alternative available for small laboratories without laboratory information management systems. To optimize the probability of reaching consensus on a single laboratory procedure recommendation the Committee first attempted to find an acceptable resolution of these concerns and/or possible revisions to the DQ FAC Single Laboratory Procedure v 2.4 before bringing it to a vote. The discussions regarding efforts to reach resolution of these concerns are summarized in the next section followed by the final decision on the single laboratory procedure.

3.7 Recommendations and Decisions on Procedure Verification

Quantitation Limit Verification Frequency Decision

The DQ FAC Single Laboratory Procedure v 2.4 procedure (and its ACIL predecessor) both had provisions for some level of verification. However, it was always understood that these provisions could be changed to whatever frequency the Committee agreed upon. Concurrent with the development of the DQ FAC Single Laboratory Procedure v 2.4, the Policy Work Group had discussions regarding the appropriate frequency with a keen awareness of the need to maintain a balance between rigor and practicality, while recognizing that important regulatory decisions will be made based in part on the reliability of estimates of detection and quantitation. While the Policy Work Group did not come up with specific recommendations, Committee members felt that this issue needed to be addressed before voting on a single laboratory procedure. Thus, the Committee discussed and considered the following recommendation.

The Committee recommends that the following be adopted into the DQ FAC Single Lab Procedure v2.4:

Section 2.10 of the ACIL procedure specifies monthly Quantitation Limit verification spikes, evaluated on a quarterly basis. Section 2.2 of revised ACIL procedure specifies a minimum of quarterly Quantitation Limit verification spikes, evaluated on an annual basis. If we went to monthly Quantitation Limit verification spikes, evaluated annually this would provide a minimum of 24 Quantitation Limit spikes over a two year period to generate the long term estimate:

*2.2 Continue to collect method blanks with each batch from which data were reported and Quantitation Limit spikes for every analyte **analyzed at least monthly** (or four per twelve month period in separate batches spread across the time period during which analysis is conducted) **which ever is greater**. If multiple instruments are to be used for reporting data with the same Detection Limit and Quantitation Limit, **analyze two to six Quantitation Limit spikes per instrument per twelve month period, so that a minimum of twelve Quantitation Limit spikes are generated each year.***

*2.2.1. Evaluate your Detection Limits and Quantitation Limits at least every year using all of the spikes available in a 24 month period using the procedures described in the Sections below. All method blanks and Quantitation Limit spikes collected within a **24** month period should be used for reassessing Detection Limits and Quantitation Limits, unless there is reason to believe that the Detection Limit or Quantitation Limit changed substantially at some point during that **24** month period. In that case the most recent data may be used for the reassessment, but not less than 20 method blanks and seven Quantitation Limit spikes per instrument.*

Note: Proposed language changes shown as **Boldface – Underline**

Vote: 4 Agree, 5 Not Opposed, 12 Disagree

Not Approved

States: 4 Disagree

Labs: 4 Disagree

Industry: 4 Agree

Public Utilities: 4 Not Opposed

EPA: 1 Disagree

Environmental Community: 1 Not Opposed, 3 Disagree

Meeting #10, Decision 6.E

Majority Report

One State Caucus member and EPA believed that the frequency of verification specified in the DQ FAC Single Laboratory Procedure v2.4 represents a balance between rigor and cost. The proposed language change (despite its intent) appears to require monthly verification analyses, regardless of how frequently laboratories perform analyses on actual samples. In addition, for multi-component analyses requiring the preparation of a variety of verification samples (due to incompatibility of mixtures or concentration ranges) to evaluate the entire spectrum of analytes measured, costs of monthly verification testing could outweigh any benefits gained by generating a larger evaluation data set. It would be prudent to perform a cost-benefit analysis prior to requiring more frequent verification than originally specified in Version 2.4.

Minority Report

One of the key criticisms of the 40 CFR Part 136 Appendix B MDL procedure has been that it was developed over idealized conditions (e.g., short term, most likely with all laboratory procedures and instrumentation optimized for peak performance). The same criticism could be applied to laboratory accreditation proficiency testing, which is often done quarterly. By setting the verification equivalent to the common frequency of proficiency testing, it is highly likely that the verification will also be done under idealized conditions. One of the features the Committee caucuses agreed upon was the need for Detection Limit and Quantitation Limit estimates that reflect normal, routine operations. Increasing testing frequency to monthly would assure that laboratories could not run the verifications from idealized, non-routine conditions. Furthermore, in the third and subsequent years, quarterly testing would limit the Detection Limit and Quantitation Limit labs to eight measurements (e.g., quarterly testing for the last two years). Thus, although this would incorporate long-term variability (note this would only be true if the Detection Limit were recalculated annually, see next recommendation), the number of data points going into the estimate would only be minimally greater than the required seven replicates currently specified in the Appendix B MDL procedure. Monthly testing would increase the number of replicates to 24, which would provide a much more robust estimate of the Detection Limit and Quantitation Limit.

Quantitation Limit Verification Frequency Recommendation

Because the previous recommendation was not approved by consensus, the Committee considered a more general recommendation asking EPA to give this subject additional consideration and to publish their findings in the Federal Register for public review and comment.

The Committee recommends that EPA give additional consideration to increasing the frequency of Quantitation Limit verification and report its findings in the preamble of the Federal Register Notice and request specific comments on the final proposed frequency.

Vote: 11 Agree, 9 Not Opposed, 0 Disagree

Approved By Consensus

States: 1 Agree, 3 Not Opposed

Labs: 4 Not Opposed

Industry: 4 Agree

Public Utilities: 3 Agree, 1 Not Opposed

EPA: 1 Not Opposed

Environmental Community: 2 Agree, 1 Not Opposed

Meeting #10, Decision 6.F

The Committee discussed but could not come to consensus on the appropriate frequency for verification, as evidenced in the below majority/minority decisions and opinions. However, the Committee did come to consensus on the above recommendation that EPA should give additional consideration to the appropriate frequency for verification of Detection Limits and Quantitation Limits and that it should specifically discuss the results of its deliberations in the preamble of the *Federal Register* notice where the final procedure/s are proposed.

The Committee recommends that, as EPA considers the appropriate level of verification, it maintain a balance between rigor and practicality, while recognizing that important regulatory decisions will be made based in part on the reliability of estimates of detection and quantitation.

EPA should address specific issues/components of verification, including such aspects as:

- The details on how verification would be carried out,
- Steps for validation of initial Detection Limit and Quantitation Limit values (and indication of when new limits should be obtained – e.g., major changes to an instrument) as well as steps for verifying those limits on an ongoing basis,
- Description of the frequency of steps undertaken in the ongoing verification process (e.g., number of samples over a given period), and
- Implications of failure to meet verification criteria (e.g., invalidation of a set of samples run over a particular period).

Optional Batch Specific Verification Decision

One caucus expressed concerns over the resource burden that adoption of the DQ FAC Single Laboratory Procedure v2.4 would impose on small laboratories that do not have laboratory information systems. To remedy this problem, they asked the Committee to consider an optional batch specific verification approach to be incorporated in the single laboratory procedure.

The Committee recommends that the following language be moved into the DQ FAC Single Lab Procedure v2.4:

Blanks and Quantitation Limit spikes in each batch

- a. If the method blank exceeds the Detection Limit and a cause cannot be identified, raise the Detection Limit to the blank result for future analysis
- b. If the Quantitation Limit spike result (or Quantitation Limit spike times Quantitation Limit/spike level, if not spiking exactly at the Quantitation Limit) is less than the Detection Limit, elevate the Quantitation Limit by a factor of two and repeat the Quantitation Limit spike at the new Quantitation Limit. Repeat this until the Quantitation Limit spike is at or above the Detection Limit.
- c. If the Quantitation Limit spike result is outside the average specified accuracy, elevate the Quantitation Limit by a factor of two and repeat the Quantitation Limit spike at the new Quantitation Limit. Repeat this until the Quantitation Limit spike meets the specified accuracy criteria.

Vote: 4 Agree, 9 Not Opposed, 7 Disagree
Not Approved

States: 4 Disagree

Labs: 3 Not Opposed, 1 Disagree

Industry: 4 Not Opposed

Public Utilities: 4 Agree

EPA: 1 Disagree

Environmental Community: 2 Not Opposed, 1 Disagree

Meeting #10, Decision 6.C

Majority Report

The Industry Caucus and one member of the Laboratory Caucus do not oppose batch-specific verification where appropriate. Although a majority of industry NPDES Clean Water Act related analyses are performed by larger commercial laboratories, many are performed by small labs that do not have Laboratory Information Management Systems. Therefore, the Industry Caucus supports an option to allow batch verification to reduce record-keeping requirements as long as false positive and false negative error rates are

adequately controlled and the regulatory requirement would permit a high detection or quantitation level due to the implementation of, essentially, more stringent Measurement Quality Objectives for false positives and accuracy. The batch verification procedure proposed would meet these criteria.

The Public Utility Caucus recognizes that the proposed procedure is designed to predict a 1% false positive rate at the Detection Limit when results from unspiked blanks are normally distributed. However this Measurement Quality Objective may not be clearly met when the method does not produce numeric results or numeric results are non-normally distributed. Another issue to consider is that the vast majority of laboratories analyzing samples for Clean Water Act compliance are small.

These are usually “in-house” laboratories that perform process control testing for the discharger, e.g. dairies, sugar refineries, power plants, military bases, and public utilities, and generally only perform tests for their own facility. Such laboratories may only produce a few unspiked blanks per batch and may only run one batch on a monthly or quarterly basis. This means that it could take many years to accumulate enough unspiked blank data to determine if the laboratory were actually achieving the intended Measurement Quality Objective for the Detection Limit. The data requirements for the procedure may also create data storage and retrieval system requirements for these laboratories that otherwise would not be required. Laboratory Reagent Blanks for all method-analyte combinations would have to be stored and then periodically reviewed.

The Public Utility Caucus also believes in a proposal to allow laboratories to have two options for on-going verification. One option is to use the currently proposed procedure of storing Laboratory Reagent Blank and Laboratory Fortified Blank results. These laboratories would need to comply with Measurement Quality Objectives of an average 1% false positive rate (i.e. a result greater than the Detection Limit for Laboratory Reagent Blanks and some average recovery and precision for Laboratory Fortified Blanks, as yet unspecified. The other option is for a laboratory to comply with a more stringent set of Measurement Quality Objectives on a batch by batch basis. These laboratories would meet a 0% false positive rate for Laboratory Reagent Blanks, i.e., all Laboratory Reagent Blanks would be less than the Detection Limit for a given batch. These laboratories would need to run a single Laboratory Fortified Blank at or below the Quantitation Limit (but not above) with each batch and get a recovery within the Measurement Quality Objectives set at some future date. However, it would not be an average recovery over several batches but recovery for that single Laboratory Fortified Blank and batch. If the Measurement Quality Objective for average recovery is $\pm 50\%$, the Measurement Quality Objective for the single batch would be $\pm 50\%$.

The Public Utility Caucus and one member of the Laboratory Caucus believe that when the batch specific Measurement Quality Objectives are not met, corrective actions need to be taken and that the actions listed in a. b. and c. of the decision are appropriate for that purpose.

Minority Report

EPA and one State Caucus member noted that the DQ FAC Single Laboratory Procedure v2.4 incorporated, at the request of the Committee, provisions to allow assessment and verification of precision and accuracy at the Quantitation Limit, should Measurement Quality Objectives for those Data Quality Indicators be developed. The proposed change to the procedure did not specify how precision could be assessed or verified at the Quantitation Limit based on available batch data only. While it may be reasonable to allow provision for batch-only verification for laboratories that do not have access to a database, the details of how to verify precision and accuracy requirements may need further refinement.

One Environmental Community Caucus representative was concerned about ambiguities in how vigorously laboratories would need to be in attempting to identify causes for a method blank

exceeding a Detection Limit. A single contamination incident producing a single high blank value (or set of blanks in one or more batches) could potentially lead to establishment of a Detection Limit level that might be significantly above a level that could easily be achieved in many subsequent analyses, with sufficient attention to practices to minimize blank contamination. Because the proposed approach for addressing Detection Limit would also have implications for Quantitation Limit (i.e., raising it in cases where the Quantitation Limit spike result is less than Detection Limit), it would seem the overall approach could easily have a tendency to lead to ever-increasing Detection and Quantitation Limits, without sufficient incentive to identify and remedy causes of high blanks.

Batch Verification Recommendation

Although a specific recommendation could not be reached by consensus, the Committee did feel the concern warranted further consideration and thus proposed the following recommendation:

Batch Verification Recommendation

The Committee recommends that during promulgation, EPA include and/or develop language to incorporate batch specific verification as an option in the procedure.

Vote: 16 Agree, 4 Not Opposed, 0 Disagree

Approved By Consensus

States: 3 Agree, 1 Not Opposed

Labs: 2 Agree, 2 Not Opposed

Industry: 4 Agree

Public Utilities: 4 Agree

EPA: 1 Not Opposed

Environmental Community: 3 Agree

Meeting #10, Decision 6.D

Although the Committee could not come to consensus on how batch verification should be incorporated into the single laboratory procedure, it did agree that EPA should develop this concept further and incorporate it into the final procedure it proposes.

Detection Limit Verification and Recalculation Decision

Revision five of the ACIL procedure indicated that the laboratory was required to re-calculate its Detection Limit annually using the additional data generated during the year. This was changed in the DQ FAC Single Laboratory Procedure v2.4 to be optional. Because this change concerned some Committee members, the following recommendation was discussed and considered by the Committee.

The Committee recommends that the following be adopted into the DQ FAC Single Laboratory Procedure v2.4:
Section 1.9 of the ACIL procedure specifies annual recalculation of Detection Limit and then uses an F test to determine if the Detection Limit should be revised. Section 2.2.2 (now 2.4) of the DQ FAC Single Laboratory Procedure v2.4 allows optional recalculation of the Detection Limit, with no decision criteria provided. By making the recalculation of the Detection Limit optional it is possible that the false positive error rate using the parametric statistical test could be greater than 1%.

*2.2.2 **Recalculate** the Detection Limit using the formulas in 1.1.7. or 1.2.7.*

Note: Proposed language change shown as **Boldface – Underline**

Vote: 8 Agree, 10 Not Opposed, 2 Disagree

Not Approved

States: 1 Agree, 2 Not Opposed, 1 Disagree

Labs: 4 Not Opposed

Industry: 4 Agree

Public Utilities: 3 Agree, 1 Not Opposed

EPA: 1 Disagree

Environmental Community: 3 Not Opposed

Meeting #10, Decision 6.G

Majority Report

Section 1.9 of the ACIL procedure stipulated an annual recalculation and reevaluation of the Detection Limit. This required use (not only) of the initial estimate data (collected over a relatively short period of time), but also of the subsequent quarterly data (censored methods) or all blank data (non-censored methods) that clearly represent more long-term, routine performance. One of the criticisms of the Part 136 Appendix B MDL procedure was that it reflected only extremely short-term performance. Nothing was learned in the Pilot Study to justify dropping the recalculation requirement. If the requirement is dropped, the Laboratory Detection Limit would be marginally better than the MDL because the laboratory would not be required to use any data beyond that used for the initial short-term estimate. If laboratory performance of the method over time changed (becoming better or worse), the Laboratory Detection Limit would not reflect the laboratory's current capability unless there were a mandatory (at least) annual recalculation using all available information.

In the DQ FAC Single Laboratory Procedure v2.4, the primary control of the false positive error rate (target $\leq 1\%$) is parametric calculation of standard deviation times a constant, performed during the initial calculation and annual recalculations of the Detection Limit and Quantitation Limit. The non-parametric test is intended to catch intermittent blank outliers that may fall outside of the parametric tolerance or confidence intervals. Because the intermittent blank check is set at the 5% level, it is possible that a false positive error rate of between 1% and 5% can occur if the annual parametric recalculation is not performed prior to applying the non-parametric test.

Minority Report

The DQ FAC Single Laboratory Procedure v2.4 was refined and tested over the course of several months by a team from the Technical Work Group. Version 2.4 represented a careful balance of many factors including rigor, cost effectiveness, practicality and function. EPA and one State Caucus member were concerned that there was no discussion of changing the wording in Section 2.2.2 of the

v2.4 procedure amongst the Technical Work Group prior to the 10th Committee meeting, nor was there any justification presented at the meeting for doing so. At the very least, the rationale for the suggested change should have been presented along with an assessment or discussion of the ramifications associated with making recalculation of the Detection Limit mandatory every time verification is performed.

3.8 Decision on Single Laboratory Procedure

Single Laboratory-Determined Detection and Quantitation Limit Decision

After trying to address the issues related to verification through the recommendations that were discussed above, the Committee turned to a discussion and vote on the single laboratory procedure recommendation with those resolutions in mind.

The Committee recommends that EPA promulgate the DQ FAC Single Laboratory Procedure v2.4 recommended by the Committee for individual laboratories to determine their Detection and Quantitation Limits. The DQ FAC Single Laboratory Procedure v2.4 shall be used instead of the current MDL procedure in 40 CFR Part 136, Appendix B, for calculating all future Laboratory Detection and Quantitation Limits. The DQ FAC Single Laboratory Procedure v2.4 has the following two capabilities:

- Demonstrates the laboratories performance at a specified level.
- Determines the lowest possible value achievable by the laboratory while meeting the Measurement Quality Objectives.

Vote: 14 Agree, 1 Not Opposed, 5 Disagree
Not Approved

States: 4 Agree

Labs: 3 Agree, 1 Disagree

Industry: 4 Agree

Public Utilities: 2 Agree, 1 Not Opposed, 1 Disagree

EPA: 1 Disagree

Environmental Community: 1 Agree, 2 Disagree

Meeting #10, Decision 6.A

Majority Report

The original ACIL procedure was modified prior to the Pilot Study to incorporate Pilot Study Measurement Quality Objectives for precision, bias and false negative protection. It was also modified slightly to take advantages of some of the strengths of the Consensus Group Detection Limit procedure, which was similar to the ACIL procedure in many ways, so that both procedures would not need to be included in the Pilot Study. The most substantial modification was using a "k" factor in place of a Student "t" factor for calculation of the uncensored Detection Limit. The ACIL procedure, with modifications indicated by the Pilot Study results and informed by concepts from the Consensus Group and Laboratory QC procedures, was recommended for a single laboratory Detection/Quantitation Limit procedure, (DQ FAC Single Laboratory Procedure v2.4). These modifications included Measurement Quality Objective flexibility while maintaining false negative protection, an optional procedure for the determination of the "lowest possible Quantitation Limit" and a procedure to protect against intermittent blank contamination.

A majority of the Committee recommends that EPA adopt the modified ACIL Single Laboratory Detection/Quantitation Limit procedure to replace the 40 CFR, Part 136 Appendix B (MDL) procedure and

the minimum level (ML), because of its superior performance. The ACIL procedure, as demonstrated in the Committee Pilot Study achieves or addresses all of the criteria which the Committee identified as critical for a single laboratory detection and quantitation procedure. The resulting DQ FAC Single Laboratory Procedure v2.4 is robust and achieves all of the FAC objectives for a single laboratory procedure.

Procedure Performance

Overall, the ACIL procedure performed better in terms of achieving targeted false positive and false negative rates than other procedures under consideration in the Pilot Study. Some weaknesses of the procedure were identified, and a work group made several modifications to the procedure to address these weaknesses. As a result, the modified ACIL procedure (DQ FAC Single Laboratory Procedure v2.4) is stronger in the way that verification is performed and in handling of non-normal data and intermittent blank contamination issues.

Comparison with “What we need a procedure to do”

Early in the Committee process, the Committee identified a number of properties that a successful detection/quantitation procedure should have. These criteria were identified in the “What we need a procedure to do” document. The modified ACIL procedure (DQ FAC Single Laboratory Procedure v2.4) addresses all of these criteria, except for determination of inter-laboratory Detection Limits, which is, of course, not required for a single laboratory procedure. (The modified ACIL procedure can be applied on a multi-laboratory basis.) In particular, the modified ACIL procedure (DQ FAC Single Laboratory Procedure v2.4) addresses those criteria that are not met by the current MDL procedure. These weaknesses of the current MDL, which were the primary reason for the formation of the Committee, include failure to provide explicit estimates for precision and bias at the Quantitation Limit; lack of verification of false positive and false negative rates; lack of requirement to meet qualitative identification criteria defined in the analytical method; failure to incorporate routine variability; and failure to address situations where blanks have a non-zero response.

Ease of Adoption

The modified ACIL procedure (DQ FAC Single Laboratory Procedure v2.4) has some similarities to the current MDL that should result in easy adoption. In particular, the startup determination involves method blanks (which laboratories will already have for most method/analyte combinations,) and spikes at or below the proposed Quantitation Limit, which laboratories will also have from their existing MDL studies. It is important to recognize that for uncensored methods, laboratories will be able to define and calculate Detection and Quantitation Limits using the modified ACIL procedure without any need for additional analytical work. For censored methods labs existing MDL data can normally be used for the initial estimate of the Detection Limit.

The modified ACIL procedure is also similar in key respects to the drinking water MRL procedure. Analytical work that has been performed to determine a MRL will also suffice to define the ACIL procedure Quantitation Limit. Conversely, work done for a startup ACIL procedure will suffice for a MRL, if the performance of the method is adequate.

Measurement Quality Objectives for relevant Data Quality Indicators, such as precision, bias, false positive and false negative error rates must be established to achieve the objectives of the Committee. The modified ACIL procedure (DQ FAC Single Laboratory Procedure v2.4) is designed to achieve these and provides flexibility in that different specifications for precision and accuracy are easily accommodated, for methods and/or analytes with differing performance.

Additional Considerations

- The procedure is written in such a way as to allow an adequate Quantitation Limit to be derived which meets laboratory, user and regulatory needs without excessive costs. If a lowest possible Quantitation Limit needs to be developed for a particular need (at an additional expense), a provision

has been included in section 1.2.2.1 to allow for this.

- Adequate space is maintained between the Detection Limit and Quantitation Limit to protect against false negative errors (i.e. saying that an analyte is absent when it is actually present). The more precise and accurate the method the narrower the gap between the Detection Limit and Quantitation Limit. This provision allows a wide range of Measurement Quality Objectives for precision and bias (Measurement Quality Objective flexibility), while still protecting against false negative errors. False negative protection at about the five percent level is targeted, which is akin to the IUPAC L_D .
- Recommendations regarding reduction of laboratory contamination are incorporated into the procedure. Laboratories with lower levels of laboratory contamination will be able to achieve lower Detection Limits and Quantitation Limits, thus allowing the market forces to drive them to reduce the level of cross contamination in the laboratory.
- The procedure was also designed to generate realistic Detection Limit and Quantitation Limit estimates based on routine laboratory performance. This had been one of the major criticisms of the MDL and was the primary reason why the USGS developed the Long Term MDL (LT-MDL). The single laboratory procedure has been designed specifically to produce long term estimates with periodic verification of those estimates, to assure that the Detection Limit and Quantitation Limit estimates represent the routine performance of the laboratory.
- Initial estimates for Detection Limit for uncensored methods are based on a "K" factor (tolerance interval) as opposed to a "t" factor (confidence interval) to provide a better estimate of long term variability using short term data. Once long term data is collected the "K" factor is no longer needed. The use of K over t was decided because the Pilot Study data and long term datasets indicated that it provided a better estimate of long term variability and did a superior job in achieving the Committee objective of less than or equal to a one percent false positive error rate at the Detection Limit.
 - The Committee Pilot Study report concluded that the modified ACIL procedure using a k factor to derive the Detection Limit for uncensored methods, did the best job of achieving the targeted false negative error rate of 1% or less.
 - Historical blank data from method 200.7 for 27 metals yielded a long term false positive error rate of approximately 2% when using a t factor to determine the short term estimate (n = 7) vs. a 1.2% false positive error rate when using a K factor.

Minority Report

EPA supports most of the elements of the new single laboratory procedure for detection and quantitation, however, EPA has two principal concerns:

1. Student t vs. K Factor

The Student t factor is used throughout the procedure for detection and quantitation calculations except when uncensored methods are at issue such as trace metals analyses. If a K factor is used, value can be as much as 94% larger than if a Student t factor is used for seven samples. This higher multiplier would result in higher Detection Limits, which would decrease the ability to detect the analyte of interest and therefore increase the rate of false negatives. For uncensored methods, the majority believes a K factor is needed to keep false positive rates at $\leq 1\%$. EPA disagrees. Using K does not ensure that false positive rates will be consistently less than 1%. When the distribution is not normal, the false positive rate based on K may also exceed 1%; in these cases the Detection Limit would be adjusted based on ongoing verification regardless of which multiplier was originally used, and therefore there is no benefit to using K instead of Student t. The Student t factor provides adequate protection against correction for high false positives by targeting an average false positive rate of 1%, and allows for a consistent scaling factor for both censored and uncensored methods. At the same time use of the Student t factor does not increase Detection and Quantitation Limits unnecessarily.

2. False Negative Correction

The use of a false negative correction factor is used in the procedure to satisfy the concern that there be “adequate space” between the Detection and Quantitation Limits. Because the Detection and Quantitation Limits are separately derived, there may be circumstances when the DQ FAC Single Laboratory Procedure v2.4 results in a Detection Limit equal to or greater than the initially and separately derived Quantitation Limit. In these cases, the procedure requires you to increase the Quantitation Limit until it exceeds the Detection Limit by a certain amount.

EPA disagrees that this is the only or best solution to this circumstance. While there may be some desire that there be “adequate space” between the detection and Quantitation Limits to prevent false negatives, this is not required, and there are circumstances where Detection and Quantitation Limits are equivalent. Moreover, use of the false negative correction factor to provide “adequate space” unnecessarily inflates the Quantitation Limit, resulting in inadequate protection of the environment.

Having both a false negative and false positive requirement in the same procedure requires added separation of the Detection and Quantitation Limits, inflating the Quantitation Limit beyond the true quantitation value. Furthermore, raising the Quantitation Limit to meet the false negative rate Measurement Quality Objective does not mean that there is greater protection against false negatives. Instead it means that a more conservative statement is being made (i.e., you become more near-sighted) about where you can detect the analyte with high confidence. To better protect against false negatives, either the Detection Limit would need to be lowered (by calculating the Detection Limit using the Student t instead of K, for example), or a more sensitive method would need to be used.

In addition to the two concerns identified by EPA above, one member of the Environmental Community Caucus had the following additional concerns:

There is potential bias in identification of the quantitation level. For example, early discussion of a Quantitation Limit establishment (section 1.2.2) indicates that “the spiking level must be at or below the level that the laboratory intends to use as their Quantitation Limit for reporting.” This could be read to imply that a good idea for the location of a Quantitation Limit exists even before a Quantitation Limit determination is carried out, and that only verification that a particular Quantitation Limit can be attained is needed. In addition, steps 1.2.3 – 1.2.6 (involving testing a particular spike level) imply that the main concern is that a level too low may have been chosen as the Quantitation Limit, rather than a level too high – i.e., all remedies for failure to meet criteria involve increasing the spike level (and thus the Quantitation Limit). While the procedure in section 1.2.2.1 outlines an approach to identifying the lowest possible Quantitation Limit when needed, it appears the rest of the procedure could produce a Quantitation Limit that is in at least some measure arbitrary (rather than more consistent with standard definitions of a Quantitation Limit). The overall effect is the final Quantitation Limit in the general procedure may not reflect the true potential for analysis at lower levels, even absent an effort to determine the lowest possible Quantitation Limit.

There is a lack of clear rationale for use of some statistical or analytical approaches in the procedure (including via any experience in the literature). For example, in addition to questions on use of the K-statistic (as discussed by EPA), it is not clear if “Lowest Expected Result” in section 1.2.9 is an existing concept in the detection/quantitation literature.

There is an effective overall potential for over-protection against false positives at the expense of false negatives. In general, the remedies for failures to meet established criteria in the draft procedure involve raising either the Detection Limit or Quantitation Limit. (Section 2.7 of the DQ FAC Single

Laboratory Procedure v2.4 does allow for “optional” lowering of Quantitation Limit if established criteria can be met.) In some cases these remedies may make sense from a statistical perspective, but they do not sufficiently consider the underlying measurement process. Laboratory contamination problems (for example) could lead to both high Detection Limit and Quantitation Limit values – a systematic reduction in contamination would lower Detection Limit and potentially Quantitation Limit (and/or help ensure that Detection Limit was lower than Quantitation Limit). The current MDL procedure addresses contamination, in part, in noting that the analyst should “prepare reagent (blank) water that is as free of analyte as possible.” (40 CFR Part 136 Appendix B.) In addition to being consistent with good laboratory practices, a more formal recognition in the procedure of the importance of minimizing contamination would be consistent with the goal noted in Great Lakes Initiative guidance for establishing a permit Quantitation Limit (or minimum level) when a nationally promulgated limit is not available, whereby “the permitting authorities must demonstrate that any minimum quantification level specified is as close to the WQBEL as practicable.” (See Section VIII.H.2 in U.S. EPA, Water Quality Guidance for the Great Lakes System: Supplementary Information Document (SID), EPA-820-B-95-001, March 1995.)

The concerns of one member of the Public Utilities caucus and one member of the Environmental Laboratory caucus are:

The MDL should be conducted over three to five days and then repeated at a minimum of once a year. The Laboratory Detection Limit and Quantitation Limit cannot be any higher than the promulgated Detection Limit and Quantitation Limit for that method/analyte. Where a promulgated method/analyte is not available, the annual laboratory MDL cannot be any higher than the initial Laboratory Detection Limit and Quantitation Limit.

With each batch of samples, one should prepare and analyze a laboratory control spike at three to five times the Quantitation Limit. If precision is desired, then prepare and analyze the laboratory control spike in duplicate. Ideally the laboratory control spike should be at the Quantitation Limit. However, as everyone knows, some analytes have poor recoveries which would then put the quantitation below Quantitation Limit. This is not perfect but it is the best that can be done under the circumstances. What is really needed are better methods for the low recovery compounds but that is not likely to happen anytime soon.

One Public Utility Caucus member believes:

The proposed procedure is basically the same as the existing 40 CFR 136 Appendix B MDL procedure. The procedure at best predicts a 1% false positive rate when results from unspiked blanks are normally distributed. However, this condition is not met in the majority of situations where either the method produces no numeric results at all or, if numeric results are produced, they are non-normally distributed. As such, the proposed procedure does not actually produce a concentration at which a false positive rate would be 1%.

3.9 Determining a National Quantitation Limit

[Chapter 4, Uses of Detection and Quantitation in Clean Water Act Programs, presents the Committees discussion and recommendations on a National Quantitation Limit. The discussions in this chapter focus on Committee recommendations on how a National Quantitation Limit would be derived.]

Because of the regulatory significance of the recommended use of the National Quantitation Limit being considered by the Committee, it was extremely important to some caucuses that the procedure for

determining a National Quantitation Limit be defined. Unfortunately, the Technical Work Group did not have time to develop a detailed procedure. However, it did consider and bring forward some general recommendations for consideration by the Committee. These recommendations are intended to provide a framework to guide EPA in developing a detailed procedure.

The Technical Work Group and, subsequently, the Committee considered two alternative approaches to setting a National Quantitation Limit. One was an inter-laboratory procedure like the ASTM D6512-07. The other was a multi-laboratory procedure; however, there were no published multi-laboratory procedures for the Committee to consider. In discussing the merits of these two approaches, the Industry and Public Utility Caucuses expressed a desire that any procedure used for setting a National Quantitation Limit would assure that results on samples split between labs would be comparable. While those caucuses felt that one viable approach to assuring comparability between laboratories was to base a National Quantitation Limit on an inter-laboratory procedure, they felt that this could be accomplished through other means. One example was by giving the issue of comparability special attention in the method validation process.

Future Method Promulgation – Validation Studies

The Committee recommends that during the Data Quality Objective process, EPA give special attention to assuring the analytical method produces comparable results, at or near the National Quantitation Limit, on split samples, analyzed in different laboratories with the same method, and that EPA specifically describe the steps taken in the proposed rule.

Vote: 14 Agree, 3 Not Opposed, 0 Disagree, 1 Absent

Approved By Consensus

Meeting #7, Decision 4. B

This recommendation was left general to allow EPA flexibility to address the comparability issue differently for different situations and/or methods. During the discussion, it was observed that one means of assuring comparability might be in how Quality Assurance and Quality Control criteria are set, but there may also be other ways. In implementing the recommendation EPA should consider method validation studies that would specifically target comparability of results on split samples and then publish those studies when the methods are published for public comment. The adequacy of how it addressed the comparability issue would then be open for public review and comment.

At one point in its discussion of uses of detection and quantitation, the Committee entertained a process for collecting data through the Integrated Compliance Information System for the purpose of providing information to inform potential future updates of National Quantitation Limits. However, the Technical Work Group did not have time to develop general recommendations on how these data should be used to calculate future National Quantitation Limits. Because of concerns over the lack of a procedure for future updates of a National Quantitation Limit, the language pertaining to future updates was removed from further consideration.

Decision to Promulgate How National Quantitation Limits are Derived.

Given the importance of the National Quantitation Limit for reporting, compliance and enforcement, the Committee recommended that EPA promulgate how the National Quantitation Limit would be derived and suggested a number of criteria that could be considered when EPA proposes such a procedure.

The Committee recommends that EPA promulgate how a National Quantitation Limit is derived.

Vote: 7 Agree, 10 Not Opposed, 0 Disagree, 1 Absent
Approved By Consensus

Meeting #7, Decision 5.B

Because a specific procedure for how a National Quantitation Limit would be determined was not recommended by consensus, the Committee felt that it is extremely important that EPA develop and promulgate an appropriate procedure.

Decision on Recommendation of Criteria to be Considered When EPA Promulgates Quantitation Limits

The Committee recommends:

- a. EPA use the Data Quality Objective process to set target Measurement Quality Objectives for setting National Quantitation Limits for use in NPDES permit compliance testing.
- b. A minimum of 6-7 labs be used to set National Quantitation Limits.
- c. Data be collected, at a minimum, over 3- 6 months.
- d. A minimum of 20 spikes be used in the calculation of each Laboratory Quantitation Limit.
- e. The data and lab be evaluated for validity prior to acceptance.
- f. An appropriate outlier test then is applied to the dataset.
- g. The data is evaluated for normality, using standard statistical tests.
- h. If the data is normally distributed then calculate the upper 95% confidence limit, which becomes the Quantitation Limit.
- i. If the data are non-normally distributed then the 95th percentile of the Laboratory Quantitation Limit data becomes the Quantitation Limit.

Vote: 9 Agree, 8 Not Opposed, 1 Disagree, 2 Absent
Not Approved

States: 1 Agree, 2 Not Opposed, 1 Absent

Labs: 4 Not Opposed

Industry: 4 Agree

Public Utilities: 4 Agree

EPA: 1 Disagree

Environmental Community: 2 Not Opposed, 1 Absent

Meeting #10, Decision 4.H

Majority Report

This recommendation is consistent with others in that it refers to the Data Quality Objectives process to establish target Measurement Quality Objectives for NPDES compliance testing. The specification of between six and seven laboratories is consistent with well established inter-laboratory validation protocols (e.g., ASTM's D2777) and with the number of laboratories EPA has used previously in validating methods for 40 CFR Part 136. There are several reasons behind recommending that data be collected over three to six months. First, most caucuses agreed that Single Laboratory Quantitation Limits should be based on routine operations implemented by collecting data over a period of time. The procedure considered by the Committee (but not recommended by consensus) includes validation steps designed to assure that initial short-term estimates are valid. It takes time to let these validation procedures work effectively. In addition, to assure that any intermittent blank contamination is properly accounted for, the data must be collected over a suitable period of time. Most EPA methods take years to validate and promulgate, so three to six months of

data gathering will not significantly delay promulgation of new methods and will assure that the checks and validations in the single laboratory procedure have time to work properly. The specification of 20 Quantitation Limit spikes is also intended to assure that a reliable estimate of the Quantitation Limit is obtained. The references to data validation and outlier testing are appropriate checks on quality control and protection against outliers, which are self evident. The final three points deal with concerns raised by some Technical Work Group members regarding the ability to determine whether the Single Laboratory Quantitation Limits (from the small population represented if the minimum number of laboratories is used to derive a National Quantitation Limit) are normally distributed and to assure that appropriate statistics are applied. If the minimum number of laboratories is used, it will be impossible to determine whether the results are normally distributed, and the recommendation defaults to use of the 95th percentile. However, if data from a large number of laboratories are available, it may be possible to determine if it is normally distributed and, if so, to apply more powerful parametric statistics (e.g., the 95% confidence limit).

Concerns over the cost implications of this approach were raised. Clearly, as with most situations, a balance between cost and benefit must be determined.

Minority Report

In a consensus recommendation at the June, 2007 meeting, EPA agreed to develop, propose and take public comment on a procedure to develop National Quantitation Limits from individual laboratory limits. At that meeting, the Technical Work Group was charged with developing a more specific recommendation but was unable to do so. Some of the specifics of this recommendation were part of the Technical Work Group's discussions; others were sent to members of the Committee less than a week before the Committee's September 19-21, 2007 meeting. EPA has not had sufficient time to consider the specifics of this recommendation, has concerns that they were not thoroughly vetted, specifically, if they are the right criteria in all circumstances, and has concerns about EPA resource implications.

CHAPTER 4 – USES OF DETECTION AND QUANTITATION IN CLEAN WATER ACT PROGRAMS

4.1 Introduction

Any time water samples are analyzed, method Detection and Quantitation Limits are used as convenient benchmarks to conclude if an analyte is present and/or quantifiable. The Committee has adopted recommendations for the determination and use of Detection and Quantitation Limits. These limits will serve to define the minimum required performance of a laboratory, may assist in comparing performance of one method to another (facilitating selection of a method most suitable for a given use), and may define important thresholds for use in evaluating compliance.

During early discussions concerning Measurement Quality Objectives and the pilot test program design, an

Agreed, by consensus, that if or when data is reported below L_Q , then the data points that fall between L_C and L_Q would be reported, for example, as detected but not quantified (e.g., DNQ).

Vote: 19 Agree, 0 Not Opposed, 0 Opposed, 2 Absent
Approved By Consensus

Meeting #4, Decision 4.B

issue arose as to how values below the Quantitation Limit should be reported given the uncertainty associated with data below

quantitation. The DQ FAC Single Laboratory Procedure v2.4, recommended by a majority of the Committee, reports all data values, regardless of the uncertainty associated with the value, and as indicated below, the laboratory will need to retain these values for five years. However, this protocol does not address what to do with these values when they must be reported for Clean Water Act purposes. Several suggestions were made as to how to report the data, including, all values should be reported, “0” should be reported, and the values should be “flagged.” For various reasons none of these suggestions met all stakeholder needs. The Committee finally agreed to the following reporting convention:

The Policy Work Group and the entire Committee spent a considerable amount of time discussing the many issues associated with uses of Detection and Quantitation Limits in NPDES permitting that are contained in the remainder of this Chapter. Since Committee caucuses had widely divergent positions on individual “Uses” issues, the Committee decided early on that a recommendation on “Uses” would need to be a “package deal,” requiring caucuses to make trade offs between the entire set of “Uses” issues. The most current version of the working document representing this “package deal” and used during the many “Uses” discussions is contained in *Appendix E: Uses Package*. The entire set of nine recommendations contained in the remainder of this Chapter represent the culmination of the Committee’s discussions on “Uses.” These nine recommendations were intended to represent the balanced “package” discussed by the Committee over the course of this Committee. It was originally intended that one vote on all Uses recommendations would be taken; instead, five votes were tallied at the September 2007 meeting, one of which contains four parts as indicated later in this Chapter. Votes of many Committee members on individual recommendations assumed that all other components would be approved. Some of these votes and/or recommendations might have changed if it had been known that any of the other components might not be approved through individual votes. Despite the multiple votes, many Committee members view the set of nine recommendations (as proposed) in the remainder of this Chapter as one, representing a careful and delicate balance between the various competing interests and positions of individual Committee members.

Decision on Other Uses of Detection and Quantitation

The Committee tabled discussion on considering whether to make recommendations regarding the use of detection and quantitation for other uses including, but not limited to, the following:

- ambient monitoring 305(b)
- pretreatment
- non-regulatory operational monitoring
- stormwater monitoring
- other studies, such as fish tissues or biosolids characterization
- reasonable potential analysis
- effluent guidelines development
- limit derivation
- development of water quality criteria
- 303(d) listing for Total Maximum Daily Loads

Vote: 20 Agree, 0 Not Opposed, 0 Disagree
Approved By Consensus

Initially, the Committee did a preliminary review of most of the Clean Water Act programs and found potential differences in how these programs make use of method Detection and Quantitation Limits. Time did not permit the Committee to fully understand these differences so a decision was made early on to focus instead on the use of method Detection and Quantitation Limits in the National Pollutant Discharge and Elimination System (NPDES) program. As a result, the Committee affirmatively decided to table discussion and recommendations on uses of method detection and quantitation in other Clean Water Act programs.

In the end, the Committee focused on NPDES permit and compliance uses and recommends that EPA promulgate procedures for obtaining individual laboratory Detection Limit and Quantitation Limit values as well as a National Quantitation Limit value/s for specific methods.

Situations where Water Quality Based Effluent Limits (WQBELs) are less than Quantitation Limits present a challenge in setting permit limits and conditions as well as in making compliance determinations. In the absence of a regulatory requirement promulgated by EPA, state and other permitting authorities have been implementing different approaches for situations where the WQBEL is less than the identified Quantitation Limit. These include approaches for:

- Considering data reported at greater than the Detection Limit but less than the Quantitation Limit;
- Calculating monthly averages;
- Determining compliance with daily maximum limits and monthly average limits
- Reporting data; and
- Appropriate compliance response in light of data uncertainty and the need for the protection of public health and the environment.

The Committee determined that it is appropriate to use the Quantitation Limit as the threshold for determining compliance with WQBELs as this is the lowest level where the accuracy demonstrated by the laboratory is appropriate for this purpose. The Committee created the concept of a National Quantitation Limit as a key component of the “package of uses recommendations” that the Committee developed. The National Quantitation Limit would set a minimum level for use in determining compliance that permitting authorities (e.g. states) would have to implement as a Permit Quantification Limit in NPDES permits. It was

also intended to define the minimum level of acceptable performance by a laboratory analyzing wastewater for compliance determinations.

Decision on Recommendation of Criteria to be Considered when Developing a Procedure for Determining a National Quantitation Limit for Existing and Future Methods

The Committee recommends that:

- a. National Quantitation Limits be promulgated in a 40 CFR Part 122 table by analyte
- b. EPA generate National Quantitation Limits as rapidly as possible so that the Committee recommendation on permitting conditions and compliance determinations can be fully implemented.
- c. Quantitation Limits be promulgated only using the nationally promulgated approach.
- d. Methods may be promulgated without promulgating a Quantitation Limit for that method. As new methods are proposed without a promulgated Quantitation Limit, data (e.g.: Single Laboratory Detection Limits, Single Laboratory Quantitation Limits, etc.) showing demonstrated method performance should be included in the method. The methods should include a statement that these performance levels are guidance and may not always be achievable.

Vote: 16 Agree, 4 Not Opposed, 0 Disagree

Approved By Consensus

States: 4 Agree

Labs: 2 Agree, 2 Not Opposed

Industry: 4 Agree

Public Utilities: 2 Agree, 2 Not Opposed

EPA: 1 Agree

Environmental Community: 3 Agree

Meeting #10, Decision 4.G

Many of the recommendations in this chapter are dependent on a national benchmark for quantitation and the development of Detection and Quantitation Limits are closely tied with promulgation and/or revision of analytical methods. Currently the vast majority of method/analyte combinations promulgated in 40 CFR Part 136 do not have associated Quantitation Limits. Since the Committee is recommending that EPA adopt National Quantitation Limits and most method/analyte combinations do not have a nationally required Quantitation Limit, if EPA were to proceed on this path, it would need to create new National Quantitation Limits for most analyte/method combinations before the benefits of the recommendations of this chapter can be fully realized. However, the Committee expressed a desire for EPA to promulgate new, more sensitive analytical methods while it develops the data necessary to support a National Quantitation Limit. Therefore, the Committee recommends that new analytical methods be promulgated in Part 136 as quickly as is feasible, to be followed by the creation and promulgation of analyte-specific National Quantitation Limits in the permit regulation at 40 CFR Part 122.

Moreover, the Committee recognizes that significant costs and resources are associated with a study to establish a National Quantitation Limit for a particular method. Therefore, the Committee believes that EPA should focus new method promulgation (or establishment of Quantitation Limits for new methods) in situations where there are clear program needs (e.g., WQBEL's below Detection/Quantitation Limits or capabilities in current EPA approved methods).

4.2 Removal of a National Detection Limit From Uses Decisions

The Committee debated the need for a National Detection Limit and ultimately determined that there was no need for a regulatory Detection Limit similar to the National Quantitation Limit.

Need for National Detection Limits

The Committee approves the removal of National Detection Limits from the Revised Uses document.

Vote: 16 Agree, 2 Not Opposed, 1 Disagree
Not Approved

Meeting #8, Decision 1

Majority Report

As stated previously in this report, the Committee has recommended (although not by consensus) a single laboratory procedure for determining Detection and Quantitation Limits at each laboratory as well as development of National Quantitation Limits, particularly for analytes with WQBELs less than currently achievable Quantitation Limits. These recommendations are intended to establish baseline requirements for the NPDES permitting program across the nation, recognizing the benefits to regulators and dischargers of a fair and uniform way to judge compliance with numeric NPDES effluent limitations where measurements are less certain. If implemented in federal regulation, the Committee recommendations would set minimum requirements that each permitting authority would have to implement in NPDES permits.

The Committee also determined that it is appropriate to include a provision under which the permitting authority would require a permittee to take action to reduce pollutant concentrations where a pollutant in a discharge is detected but not quantified by the permittee's laboratory a "significant number" of times. The Committee decided to remove references to a National Detection Limit from the "Revised Uses Document." This decision was based, in large part, on the Committee's recognition that many laboratories would have Detection Limits below those that would be nationally promulgated and the Laboratory's Detection Limit, not a National Detection Limit, would be used to trigger additional steps to reduce pollutant concentrations. EPA may still want to promulgate a Detection Limit associated with Part 136 methods as a valuable reference point.

Minority Report

The Committee is proposing that a fixed National Quantitation Limit needs to be established for each regulated analyte where generally available Quantitation Limits are above permit limits (e.g. a WQBEL), that a Permit Quantitation Limit be established at the National Quantitation Limit and that individual laboratories need to have a laboratory specific Quantitation Limit \leq the Permit Quantitation Limit when the National Quantitation Limit is greater than a permit limit (e.g., WQBELs). The Committee is also recommending that:

- Results below the Detection Limit be reported as "not detected",
- Results between the Permit Quantitation Limit and Detection Limit be reported as "detected but not quantified at or above the Permit Quantitation Limit" and
- That "Not Detected" and "detected but not quantified at or above the Permit Quantitation Limit" results are treated for averaging purposes as zero.

For this strategy to work, the values of Quantitation Limit and Detection Limit have to be sufficiently different to allow for "detected but not quantified" to be detected. A National Detection Limit would be a ceiling on the Detection Limit that individual laboratories could report. The National Detection Limit is needed to ensure that there is adequate "distance" between the Detection Limit determined by an individual laboratory and the National Quantitation Limit. It would be counter productive to have a Detection Limit that was equal to the National Quantitation Limit, or nearly so.

The National Detection Limit is also needed to ensure equal protection to all receiving bodies with a given WQBEL and equity for all permittees discharging to receiving bodies with a given WQBEL. As the Pilot Study showed, laboratories can produce a Detection Limit with concentrations that differ over orders of magnitude. Without a National Detection Limit, it would be possible for two permittees to discharge water to a receiving body with the same concentration of an analyte. One would have to do a pollutant minimization program and the other would not, simply because of differences in the laboratory capability. In fact, with the range of differences in Detection Limits seen in the Pilot Study, it would be possible for a discharger with a higher concentration to have no pollutant minimization program whereas a discharger with a lower concentration would have to conduct a pollutant minimization program. This does not provide equal protection to all waters nor equity to permittees.

4.3 Establishing NPDES Permit Conditions and Determining Compliance

As indicated above, the Committee took a single vote on the four-part recommendation that follows. These four parts of the recommendation are presented separately as Parts 1, 2, 3, and 4 although the Committee took a single vote on the whole recommendation. The majority report begins on page 48 and the minority report on page 49.

Recommendation on Reporting Data and Determining Compliance Where the WQBEL is Less Than the National Quantitation Limit

Except in cases where the permitting authority requires use of a method more sensitive than the method for which a National Quantitation Limit exists, the Committee recommends that EPA promulgate a rule to modify 40 CFR Part 122, as follows:

Part 1

The Committee recommends the following be required where EPA has promulgated a National Quantitation Limit in 40 CFR Part 122:

- a. The default Quantitation Limit to be included in the permit or in rule as appropriate (Permit Quantitation Limit) is the 40 CFR Part 122 promulgated National Quantitation Limit unless the regulator determines that the Permit Quantitation Limit should be adjusted to account for sensitivity, selectivity, and/or matrix effects;
- b. The permit shall contain a condition that the Quantitation Limit determined by the permittee's laboratory (Laboratory Quantitation Limit) shall be at or below the Permit Quantitation Limit. The permittee's laboratory may use any 40 CFR Part 136 method for which they can demonstrate a Laboratory Quantitation Limit at or below the Permit Quantitation Limit. If matrix effects have been given special attention in the permit then they would also have to be considered in compliance and enforcement;
- c. The permit shall require the permittee to report the Laboratory Detection Limit and the Laboratory Quantitation Limit and maintain such information for a period of at least five years;
- d. The permit shall require the permittee to maintain individual numeric results for a period of at least five years. The regulator may require the individual numeric result for any value that is greater than or equal to the Laboratory Detection Limit and less than the Permit Quantitation Limit be reported in a supplemental report.
- e. The permit shall require that the Laboratory Detection Limit and the Laboratory Quantitation Limit be determined using the steps of the 40 CFR Part 136 procedure to establish the lowest possible value by the laboratory, and
- f. That EPA require the Laboratory Detection Limit, the Laboratory Quantitation Limit, and the Permit Quantitation Limit be reported by the regulator to the Integrated Compliance Information System (ICIS).

Meeting #10, Decision 4.I

Part 2

The Committee recommends the following be required where EPA has promulgated a National Quantitation Limit in 40 CFR Part 136:

- a. The permitting authority will set average and daily maximum permit limits at the WQBEL.
- b. Permittees must report to the permitting authority all information in the following manner on the Discharge Monitoring Report (DMR):
 - i) To report daily maximum sample results:
 - a. For values not detected at the Laboratory Detection Limit, report "not detected".
 - b. For values detected at the Laboratory Detection Limit but less than the Permit Quantitation Limit, report "detected less than the Permit Quantitation Limit."
 - c. For values greater than or equal to the Permit Quantitation Limit, report the actual numeric values.
 - ii) To report average sample results:
 - a. When all values used to calculate an average are not detected at the Laboratory Detection Limit, report "not detected".
 - b. When all values used to calculate an average are "detected less than Permit Quantitation Limit", report "detected less than the Permit Quantitation Limit."
 - c. When values used to calculate an average are a combination of "not detected" and "detected less than the Permit Quantitation Limit", report "detected less than the Permit Quantitation Limit."
 - d. When one or more value used to calculate an average is greater than or equal to the Permit Quantitation Limit, report the calculated numeric average after assigning zero to any individual sample result reported either as "not detected" or "detected less than the Permit Quantitation Limit".
- c. To determine NPDES permit compliance with results reported on the DMR, the permitting authority will:
 - i) Determine that any results reported as either "not detected" or "detected less than the Permit Quantitation Limit" are in compliance with the effluent limitation.
 - ii) Compare any numeric result directly to the WQBELs

Meeting #10, Decision 4.I

Part 3

The Committee recommends the following be required where EPA has promulgated a National Quantitation Limit in 40 CFR Part 136:

Permits shall include language that triggers additional steps when a “significant number” (to be determined in permitting process) of values detected at the Laboratory Detection Limit but less than the Permit Quantitation Limit are reported. These steps may include additional or accelerated monitoring, analytical studies such as matrix studies, pollutant minimization programs, or other permit conditions outside of the determination of compliance with effluent limitations. Reports under such provisions will be done outside of the DMR process, except that any additional effluent testing performed using approved analytical methods as part of the special studies must be reported on the DMR.

Meeting #10, Decision 4.I

Part 4

The Committee recommends the following be required where EPA has not promulgated a National Quantitation Limit in 40 CFR Part 136

- a. In the absence of a National Quantitation Limit, the permitting authority is free to establish it's method for determining compliance for analytes that have limits/water quality standards at a level lower than that which can be detected and/or quantified.
- b. For a list of analytes as defined by EPA, the permit shall require that the Laboratory Detection Limit and the Laboratory Quantitation Limit be determined using the steps of the 40 CFR Part 136 procedure to establish the lowest possible value by the laboratory, and
- c. That EPA require the Laboratory Detection Limit, the Laboratory Quantitation Limit, and the Permit Quantitation Limit be reported by the regulator to the Integrated Compliance Information System

Result of Vote on Parts One Through Four as a Package

Vote: 12 Agree, 4 Not Opposed, 4 Disagree
Not Approved

States: 3 Agree, 1 Not Opposed

Labs: 3 Not Opposed 1 Disagree

Industry: 4 Agree

Public Utilities: 4 Agree

EPA: 1 Agree¹

Environmental Community: 3 Disagree

Meeting #10, Decision 4.1

(1: EPA voted as the Office of Water)

Majority Report

These four majority recommendations contain the specifics of how NPDES data reporting and compliance determinations would be made in situations where the WQBEL is less than the National Quantitation Limit. The majority hopes that these recommendations will promote more uniformity and equity in reporting and compliance determinations across the country, resulting in efficiencies for permitting authorities and regulated parties alike. Besides the WQBEL, two benchmarks, the Permit Quantitation Limit and the Laboratory Detection Limit, are critical to implementing these majority recommendations. The Permit Quantitation Limit in the NPDES permit would be the National Quantitation Limit promulgated in 40 CFR Part 122 unless the permitting authority determined that the National Quantitation Limit did not adequately account for differences in selectivity and sensitivity that are characteristic of the discharge matrix of the permittee. In that case, the permitting authority would adjust the Permit Quantitation Limit to account for these matrix effects, and reporting and compliance determinations would adjust accordingly. As indicated earlier in this Chapter, the Laboratory Detection Limit was chosen instead of a National Detection Limit because it was thought that laboratories would have Detection Limits below those that would be nationally promulgated. Laboratories would establish Detection (and Quantitation) Limits using the steps of the 40 CFR Part 136 procedure to establish the lowest possible value. This would be done by applying the applicable steps in the procedure multiple times, such as iterative spiking at lower concentrations, or decreasing contamination in the laboratory's blank samples.

As previously stated, in the absence of a federal regulation regarding requirements for Detection and Quantitation Limits and their uses, states have implemented different approaches to address the situation where a WQBEL is less than the achievable Quantitation Limit. In deference to these existing state approaches, the Committee recognizes that, where authorized or not prohibited by law, any state or other permitting authority could adopt provisions that would go beyond the requirements recommended by the Committee. This is done with the understanding that entities that have been delegated the NPDES program from EPA have the authority under the Clean Water Act to adopt regulatory provisions that are different, but no less stringent than, those required under federal regulations. Such provisions would operate in lieu of the this four-part one recommendation and could include a Quantitation Limit value adopted by the state (State Quantitation Limit) lower than the nationally promulgated National Quantitation Limit. In that case, the State Quantitation Limit adopted by a delegated state would be used for determining compliance, reporting, and other applicable requirements.

In deciding how to approach the calculation of the monthly average, the Committee needed to decide how to treat values between detection and quantitation. The Committee recognizes that analytical results have a higher level of uncertainty where an analyte is detected at or above a Laboratory Detection Limit but below the Permit Quantitation Limit (detected less than the Permit Quantitation Limit) but that the science suggests they are unlikely to be zero. Given this uncertainty, assigning a non-zero value where an analyte is detected

less than the Permit Quantitation Limit (DLPQL) would have significant compliance and enforcement implications. The Committee developed a coupled approach for determining compliance and responding to DLPQL values as described in the above recommendations.

The Committee considered the recommendation that EPA promulgate a rule to modify 40 CFR Part 122 to incorporate the above recommendations. Should the permitting authority require use of a method more sensitive than the method for which a National Quantitation Limit exists, the above recommendations would not apply.

It may take many years for EPA to promulgate National Quantitation Limits for analytes with WQBELs less than currently achievable Quantitation Limits. Therefore, the situation where there is no promulgated National Quantitation Limit must be addressed. In this case, the Committee did not find it practical to establish requirements for determining compliance and suggests that the permitting authority be free to use its own process in this situation. However, the Committee believes that it is imperative that any new 40 CFR Part 136 procedure for determining the Laboratory Detection Limit and Quantitation Limit be implemented for all methods/analytes based on its determination that the new procedure will provide results at a higher level of confidence than those using the current MDL approach. In addition, reporting of data generated using the new procedure is important to provide EPA with information that it can use to set priorities for modifying existing methods or developing new methods to improve laboratory Detection and Quantitation Limits.

Minority Report

Reporting of Detected but Not Quantified Values - The proposal would entail narrative reporting (e.g. “detected less than the Permit Quantitation Limit”) in lieu of actual values for detected concentrations below the Quantitation Limit on the Discharge Monitoring Report. Such values (i.e., detected but not quantified, or DNQ) have a high probability of truly being non-zero results, and yet, in the proposal, would be reported only at the discretion of the permitting authority, on a supplemental report. This proposal would likely have the overall effect of providing less information to permitting authorities in general (including to EPA), information which could otherwise be potentially useful in several ways. For example, such data could be useful in assessing progress in reducing pollutants to non-detectable levels via implementation of pollutant minimization plans. (For example, see discussion in Section VIII.H.4 in U.S. EPA, Water Quality Guidance for the Great Lakes System: Supplementary Information Document, EPA-820-B-95-001, March 1995.)

Calculating and Reporting Average Sample Results and Use of Zero - The proposal included a provision to report “detected less than the Permit Quantification Limit” in cases where samples show a mix of not-detected and detected not quantified values, as well as a provision to obtain numeric averages only in cases where at least one value was quantified, and with all non-quantified results assigned zero. This approach is different from more commonly used practices in the scientific literature, where it has long been recognized that substitution of zero in cases of not detected or not quantified values will bias an average low. For example, for an analyte whose measured value is occasionally above the Quantitation Limit but where zero is reported for more numerous instances of hits below Quantitation Limit, the average will be artificially lowered, resulting in lower apparent loads and less protection of a water body. The general practice of assigning zero to non-detects can lead to the “virtual absence” of the analyte from a data set. (See Currie, L.A., 2004, *Applied Radiation and Isotopes*, 61:145-149).

Reporting of Low-Level Data and Uncertainties - There is recognition in the scientific community of the value in reporting low-level data and associated uncertainty. (See, for example, discussion in Currie, L.A., 1999, *Anal. Chim. Acta.* 391:105-126 and Currie, L.A., 1999, *Anal. Chim. Acta.*

391:127-134.) Currie (2004) further states, “There is near universal agreement that results of measurements and their uncertainties should be reported for *all* experimental data, including data in the region of the Detection Limit and below (ASTM, 1997, 2000; ISO, 1993; IUPAC, 1998).” (emphasis in original)

A recommendation to use zero in averaging is not consistent with EPA guidance in the Great Lakes. In the compliance provision of the Great Lakes Initiative, EPA allowed permitting authorities the discretion to use their own averaging procedures (which may include, for example, assigning zero or one-half the quantitation level for values below Quantitation Limit). Furthermore, the total maximum daily load provision of the Great Lakes Initiative indicates it is acceptable (to EPA) to assign zero values to sample data only in cases where all values are below the Detection Limit (40 CFR Part 132 Appendix F, Proc. 3). In other cases, EPA guidance indicates that “States and Tribes are required to use commonly accepted statistical techniques...” that can include the use of default values such as one-half the Detection Limit or the mid-point between Detection Limit and Quantitation Limit, as appropriate (Section VIII.C. in U.S. EPA, 1995, *Op. Cit.*)

Additional Permit Requirements - The draft proposal included language stipulating that additional steps would be required when “a ‘significant number’ (to be determined in permitting process) of values detected at the Laboratory Detection Limit but less than the Permit Quantification Limit are reported.” These additional steps could – but would not necessarily – involve incorporation of a pollutant minimization plan provision in the permit. In contrast, the Great Lakes Initiative requires inclusion of a pollutant minimization plans in initial issuance of a permit in cases where the WQBEL for an analyte is less than the Quantitation Limit. In addition, in these situations the Great Lakes Initiative also requires a re-opener clause which authorizes modification or revocation and reissuance of a permit if new information indicates the presence of a pollutant above the WQBEL (40 CFR Part 132, Appendix F, Proc. 8); this is slightly more stringent than the proposed Committee permitting strategy.

Potential for Non-Compliance - The potential for increased non-compliance in a situation where values less than Quantitation Limit are reported should be addressed through alternative compliance and enforcement strategies, rather than simply minimized through an inappropriate data censoring process. Measurement uncertainty should be considered in these situations, drawing on accepted protocols. (See, for example, the International Standards Organization Guide to the Expression of Uncertainty in Measurement.) Alternative compliance and enforcement strategies (which could include provisions so that single samples, for example, do not trigger enforcement actions) could include, for example, additional and/or more targeted monitoring of effluents or internal streams, fish tissue or other biota if appropriate, or re-examination of the pollutant minimization plans and proposal of additional research measures or practices to further reduce the pollutant load.

4.4 Alternative Test Procedures Program Compliance

The Committee did not develop specific recommendations to EPA on updating the Alternative Test Procedures Program. The Committee, however, does recommend that the Alternative Test Procedures Program be updated to be consistent with recommendations from this document.

Vote: 20 Agree, 0 Not Opposed, 0 Disagree
Approved By Consensus

Meeting #10, Decision 4.C

Under the Alternative Test Procedures Program, an organization may submit an application for approval of a

modified version of a Part 136 method or for approval of a new method to be used as an alternate to a Part 136 method.¹ The submitting organization is responsible for validating the new or modified method. EPA reviews the Alternative Test Procedure Program validation package and, if approved, subsequently promulgates the approved Alternative Test Procedure Programs in Part 136. The Alternative Test Procedure Program and rulemaking processes make demands on limited EPA methods-related resources, and, as such, approval of Alternative Test Procedure Programs can take many months and two years or more to promulgate the approved method in Part 136. Initially, the Committee intended to address some of the shortcomings of the Alternative Test Procedure Program but did not have time to do so. However, because Alternative Test Procedure Program methods and EPA-validated methods are accorded equal status once they are promulgated in Part 136, the Committee believes recommendations in this report should apply equally to Alternative Test Procedure Program methods promulgated in Part 136.

4.5 Great Lakes Initiative Compliance

The Committee recommends that its recommendations should not supersede the current Great Lakes Initiative provisions. The Committee believes that there is not a significant conflict between the Committee recommendations and the Great Lakes Initiative.

Vote: 20 Agree, 0 Not Opposed, 0 Disagree
Approved By Consensus

Meeting #10, Decision 4.A

In 1995, EPA and the Great Lakes States agreed to a comprehensive plan to restore the health of the Great Lakes. The Final Water Quality Guidance for the Great Lakes System, also known as the Great Lakes Initiative, includes criteria for states to use when setting water quality standards for 29 pollutants. The Great Lakes Initiative, like this Final Report, recognizes and addresses the scenario where WQBELs are below the Quantitation Limit of the most sensitive method. In these situations the Great Lakes Initiative provides for compliance determinations below the Quantitation Limit and for pollutant minimization plans similar to the Committee recommendations in this Final Report.

¹ Requirements for approval of alternate analytical techniques (methods) are specified at 40 CFR 136.4 and 136.5 for wastewater methods

CHAPTER 5 – MATRIX EFFECTS

5.1 Introduction

Several stakeholder caucuses expressed concern over how matrix effects can adversely impact the performance of some analytical methods, including the possibility that Detection and Quantitation Limits based on reagent water could not be achieved in real world samples. Questions with respect to how matrix effects should be addressed included how they should be accounted for in method development, how a matrix effect should be demonstrated, and how, or if, a matrix-specific Detection or Quantitation Limit would be determined. Due to the absence of effective federal guidance, states issuing permits are confronted by these issues and some have attempted to develop state guidance. However, this approach leads to inconsistencies and makes it harder for permittees and laboratories to address the issue.

Although there was interest in addressing matrix effects, there was insufficient time for the Committee to develop specific recommendations. Rather than leave the issue unaddressed, several general recommendations were formulated and considered. This generally involved EPA developing guidance in specified areas and, to the extent time allowed, identifying some specific issues that should be addressed. The formulation of these recommendations in the form of guidance instead of regulations was a conscious choice, given the difficulty of writing regulatory language for a topic that really needs to allow for some flexibility and professional judgment, and a more basic question about whether such a regulation would be appropriate. Four recommendations considered by the Committee and the outcome of the voting follow.

5.2 Matrix Effects: Discussion and Decisions

Matrix Effect Decision #1

The Committee recommends that EPA publish new guidance on matrix effects. At a minimum, the guidance should outline the appropriate level of matrix effects validation necessary for method promulgation for analytical methods to be considered for 40 CFR Part 136. The Committee recommends that EPA adhere to this guidance in methods it develops and validates for promulgation in 40 CFR Part 136. This guidance should also address the following:

- Determining the appropriate number of matrices to take into account.
- The level of validation required verses the proposed scope of use for the analytical method.
- Matrix effects validation in the Alternative Test Procedures Program.
- Impacts for consensus standards methods considered for part 136.

Vote: 10 Agree, 7 Not Opposed, 3 Disagree

Not Approved

States: 4 Not Opposed

Labs: 1 Agree, 1 Not Opposed, 2 Disagree

Industry: 4 Agree

Public Utilities: 4 Agree

EPA: 1 Disagree

Environmental Community: 1 Agree, 2 Not Opposed

Meeting #10, Decision 8.A

Majority Report

Many methods currently promulgated in 40 CFR Part 136 demonstrate poor performance when applied to real world samples, thus creating the problems that permit writers and permittees face when permit compliance testing is required. If greater attention to testing the ruggedness of a proposed Part 136 method were given during method development and validation, better methods would be promulgated, thus beginning to mitigate these issues in the future. However, it is impractical to validate a method for all possible matrices, so a trade-off between thorough ruggedness testing and cost benefit is warranted. Implementation of the proposed Committee recommendation would provide guidance and a framework for both EPA and third party method developers. The recommendation would provide EPA a great deal of flexibility in determining the correct balance between characterizing method performance and cost. The overall reasoning behind the recommendation is to generally improve the quality of methods that are promulgated, thereby reducing future difficulties in permitting.

Minority Report for Matrix Effects Decisions #1-#4 is on page 57.

Matrix Effect Decision #2

The Committee recommends that EPA develop a consistent protocol on how to demonstrate matrix effects. The Committee believes such a protocol should be sensitive to cost and required level of effort to ensure that it is applied consistently.

Questions to be addressed by the protocol:

- What level of effort is necessary to determine if the matrix effects can be resolved by modifications of the analytical method that are within the flexibility allowed within the method?
- What set of experiments and data interpretation framework would suffice to demonstrate a matrix effect if performed properly?
- Who should be responsible for implementing a procedure to determine a matrix specific Quantitation Limit?
- How broadly applicable shall a matrix effect be considered? What level of demonstration should be considered adequate for a single facility? What level of demonstration should be undertaken to extend the matrix specific Quantitation Limit to other like wastewaters?

Vote: 13 Agree, 6 Not Opposed, 1 Disagree
Not Approved

States: 3 Agree, 1 Not Opposed

Labs: 2 Agree, 2 Not Opposed

Industry: 4 Agree

Public Utilities: 3 Agree, 1 Not Opposed

EPA: 1 Disagree

Environmental Community: 1 Agree, 2 Not Opposed

Meeting #10, Decision 8.B

Majority Report

Such a protocol could be used by EPA during method validation to evaluate ruggedness of the performance of an analytical method on different types of sample matrices. Similarly, the protocol could be a useful guidance document for third party method developers (e.g., consensus organizations or anyone submitting an Alternate Test Procedure application). If a standardized protocol were available, interested stakeholders would know what needed to be done and could elect to undertake the required testing to submit to EPA. The standardized protocol would assure that if the protocol were followed, EPA would consider the data, thus leveraging EPA resources with stakeholder resources. The protocol could also be used by permittees petitioning for consideration of matrix effects during the permitting process. Having one set of guidance applied across the nation would facilitate comparability and consistency and could result in cost savings and efficiency. Furthermore, it would help ease the burden on states and/or permit writers.

Minority Report for Matrix Effects Decisions #1-#4 is on page 57.

Matrix Effect Decision #3

The FACDQ recommends that EPA develop a procedure for determining matrix-specific Detection or Quantitation Limits for use where appropriate. Again, such a protocol should be sensitive to cost and required level of effort.

Questions that should be addressed include:

- Who should be responsible for implementing a procedure to determine a matrix specific Quantitation Limit?
- How broadly applicable shall a matrix effect be considered?
- What level of demonstration should be considered adequate for a single facility?
- What level of demonstration should be undertaken to extend the matrix specific Quantitation Limit to other like wastewaters?

Vote: 11 Agree, 8 Not Opposed, 1 Disagree

Not Approved

States: 2 Agree, 2 Not Opposed

Labs: 2 Agree, 2 Not Opposed

Industry: 4 Agree

Public Utilities: 3 Agree, 1 Not Opposed

EPA: 1 Disagree

Environmental Community: 3 Not Opposed

Meeting #10, Decision 8.C

Majority Report

Regulations such as the Great Lakes Initiative provide for the possibility of a matrix-specific quantitation level in a permit but fail to provide instruction or guidance on how such a limit would be determined. Federal guidance on this topic would facilitate comparability and consistency. Comparability across the country would allow permittees and permit writers to consider data on a similar source developed in another jurisdiction, thus potentially saving costs. Consistency would make it easier and more cost effective for permittees to generate required data.

Minority Report for Matrix Effects Decisions #1-#4 is on page 57.

Matrix Effect Decision #4

When considering future updates of a National Quantitation Limit, the Committee recommends that EPA take into consideration any experience with the performance in different matrices.

Vote: 11 Agree, 4 Not Opposed, 5 Disagree
Not Approved

States: 2 Agree, 2 Disagree

Labs: 2 Agree, 2 Disagree

Industry: 4 Agree

Public Utilities: 3 Agree, 1 Not Opposed

EPA: 1 Disagree

Environmental Community: 3 Not Opposed

Meeting #10, Decision 8.D

Majority Report

At various times during deliberations, Committee members expressed concern over the fact that EPA has not updated any analytical procedures promulgated in 40 CFR Part 136 and a concern that similar problems will exist for any promulgated Quantitation Limits. EPA expressed interest in approaches to updating National Quantitation Limits in the future, although the Committee offered no specific recommendation on how this should be accomplished. However, given EPA's expressed interest in procedures for possible future updates, this recommendation expresses the common sense notion that what is learned about a method performance and/or limitations (e.g., with respect to matrix effects) through the benefit of using the procedure over time, should not be ignored when considering future updates of National Quantitation Limits. The recommendation leaves it to EPA to determine how it should consider such information and how, or if, it should effect the update of a National Quantitation Limit. It does not state that the National Quantitation Limit must be set at the highest Quantitation Limit observed in any given matrix. However, if experience shows that many industries or municipalities cannot achieve the National Quantitation Limit in their matrices, EPA may want to reconsider whether it would be appropriate to update the National Quantitation Limit based on reagent water if doing so would only exacerbate the already evident problems.

Minority Report on Matrix Effect Decisions #1-#4

Two members of the Laboratory Caucus are concerned about Matrix Recommendation #1 in that additional demonstrations on different matrices would have a negative impact on the ability of EPA to quickly incorporate new and improved methods in 40 CFR Part 136.

Two State Caucus members and one Environmental Laboratory Caucus member are concerned about Matrix Recommendation #4. If promulgated, National Quantitation Limits are presented as a single benchmark that laboratories across the nation must achieve when analyzing samples for compliance determinations. In that context, a wide spectrum of matrices (and potential matrix effects) is conceivable. Some effluent matrices may have no adverse effect on the ability of laboratories to quantify contaminants at the National Quantitation Limit, whereas other matrices may contribute to analytical interference or "noise." It appears impractical that EPA could consider all possible matrix effects in various discharges when promulgating a National Quantitation Limit for nationwide applicability. The Committee's 'Uses' recommendations gave latitude to the permitting authority to consider matrix effects when setting permit monitoring conditions, including required Quantitation Limits for reporting. It seems more practical to consider matrix effects when setting permit conditions where the matrix is demonstrated to be problematic in achieving required Quantitation Limits.

The EPA is concerned about all four matrix-related recommendations based on concerns about

resources and the difficulty of developing the recommended guidance. The core recommendations of the Committee – pilot test the new single laboratory procedure, promulgate and implement new rules incorporating the single laboratory procedure, propose an algorithm for determining the National Quantitation Limit, and define the uses of detection and quantitation in compliance and enforcement of NPDES permits – will require significant EPA resources over the next several years. At this time, EPA cannot commit additional resources to several of the other recommendations of this report, including those on matrix effects, until these core recommendations are implemented.

Additionally, EPA is concerned about the need to account for individual industry matrix effects when developing National Quantitation Limits and about the difficulty of developing matrix guidance¹ for individual NPDES permits that would work well in almost all situations. Currently, there are about 55 large categories of industrial facilities composed of 450 industrial subcategories, representing about 70,000 permitted facilities. This does not account for the over 16,000 publicly owned treatment works that must be permitted and may also have matrix effects issues

The complexity inherent in having many matrices in the NPDES program would affect permittees who would consider matrix effects in reporting compliance results whenever EPA used matrix effects to develop National Quantitation Limits.

¹EPA has a guidance document on matrix effects that is more general than that proposed by the matrix effects recommendations. This guidance document, known as the “Pumpkin Book,” allows a user to demonstrate and mitigate against matrix effects.

CHAPTER 6 – RECOMMENDATIONS ON OTHER ISSUES

6.1 Introduction

During the latter meetings of the Committee, the Committee began to consider additional issues that needed to be addressed to maximize the success of any EPA-adopted Committee recommendations. This resulted in additional recommendations that, if implemented, would:

- Ensure consistency of procedures for detection and quantitation across EPA programs;
- Engender confidence in the procedures through post promulgation performance confirmation;
- Have EPA continuing its leadership role in the development of analytical methods and providing necessary resources to develop new high quality methods;
- Have EPA establish Data Quality and Measurement Quality Objectives for the use of detection and quantitation in Clean Water Act programs and consider addressing other Clean Water Act programs such as 303(d) listings and NPDES effluent limit determination; and
- Have EPA develop guidance for implementing the new procedures and computer applications to assist in calculation of Detection and Quantitation Limits.

6.2 Implementation of Committee Procedure in all EPA Programs Referencing 40 CFR Part 136

To maintain consistency and minimize effects on the environmental laboratory community, the Committee recommends that EPA programs that reference the present Part 136 Appendix B procedure consider adopting DQFAC Single Lab Procedure v2.4 that would replace it.

Vote: 20 Agree, 0 Not Opposed, 0 Disagree

Approved By Consensus

Meeting #10, Decision 5.D

The purpose for this vote was to emphasize the importance of consistency across programs since; otherwise, there will be situations where the same analytical method at the same laboratory has different Detection Limits depending on the program. Maintaining more than one Detection Limit procedure would also be complex, costly and confusing for data users and the laboratory community.

6.3 EPA Leadership Role in Developing New Analytical Methods

The Committee recommends that EPA continue to act as the national lead for Clean Water Act programs in developing analytical methods and setting the performance standards for those methods.

Vote: 20 Agree, 0 Not Opposed, 0 Disagree

Approved By Consensus

Meeting #10, Decision 5.A

6.4 EPA Target Resources for Analytical Methods Where Most Needed

The Committee recommends that EPA evaluate the federal resources dedicated to developing analytical methods with Detection/Quantitation Limits of sufficient quality (i.e., meet Data Quality Objectives) and capable of meeting the needs of Clean Water Act programs (e.g., quantitation at or below current water quality standards) and adjust those resources, where necessary, to meet data quality and program needs.

Vote: 19 Agree, 0 Not Opposed, 0 Disagree, 1 Abstain (EPA)

Approved By Consensus

Meeting #10, Decision 5.B

6.5 Evaluate and Define Uses of Detection and Quantitation in Other Clean Water Act Programs

The Committee recommends that EPA evaluate and modify the uses of data in Clean Water Act programs (beyond those uses discussed in the Committee recommendations) based on data uncertainty and decision error rate requirements relative to corresponding Detection and Quantitation Limits. This could be accomplished through establishment of and adherence to data quality objectives for all Clean Water Act programs. How data relative to detection and quantitation limits are to be used in 303(d) listings, reasonable potential determinations, NPDES effluent limit derivation, the development of water quality criteria, and other uses should be documented.

Vote: 13 Agree, 6 Not Opposed, 1 Disagree

Not Approved

States: 1 Agree, 3 Not Opposed

Labs: 1 Agree, 3 Not Opposed

Industry: 4 Agree

Public Utilities: 4 Agree

EPA: 1 Disagree

Environmental Community: 3 Agree

Meeting #10, Decision 5.F

Majority Report

This recommendation emphasizes that, regardless of which Measurement Quality Objectives are adopted for Clean Water Act programs, data will have uncertainty based on the reliability of samples collected and analyses performed. As data uncertainty increases and all other variables remain constant, the error rate of regulatory decisions will increase. Uses of data in Clean Water Act programs will be limited by decision error, but EPA has not formally adopted decision error rate requirements for various Clean Water Act data uses. The Committee recommends that EPA adopt decision error rates for Clean Water Act data uses, relative to Detection and Quantitation Limits, and that these error rates consider data uncertainty. Data uncertainty can be defined, in part, by Data Quality Indicators and Measurement Quality Objectives, but EPA also has not adopted Data Quality Indicators and Measurement Quality Objectives for data at relevant Detection and Quantitation Limits. Another approach to address data uncertainty is through the use of confidence intervals for each data point. It is also recommended that requirements for data uncertainty and the corresponding decision error rates be documented for states and EPA regional offices using data to make regulatory

decisions pertaining to such activities as 303(d) listings; reasonable potential determinations; NPDES effluent limit derivation, compliance, and enforcement; development of water quality criteria and any other uses in Clean Water Act programs.

Minority Report

The EPA voted to disagree with the recommendation that EPA *Evaluate and Define Uses of Detection and Quantitation in Other Clean Water Act Programs* based on concerns about resources. The core recommendations of the Committee – pilot test the new single laboratory procedure, promulgate and implement new rules incorporating the single laboratory procedure, propose an algorithm for determining the National Quantitation Limit, and define uses of detection and quantitation in compliance and enforcement of NPDES permits – will require significant EPA resources over the next several years. At this time, EPA cannot commit additional resources to several of the other recommendations of this report, including the recommendation that EPA *Evaluate and Define Uses of Detection and Quantitation in Other Clean Water Act Programs*, until these core recommendations are implemented.

CHAPTER 7 – IMPLEMENTATION

7.1 Introduction

The Committee expects that EPA will proceed to develop proposed rules amending 40 CFR Parts 122 and 136 that implement the recommendations of the Committee. While the Committee did not reach consensus on all issues, the record of the Committee's extensive work and discussion of the issues will provide EPA with useful information as EPA considers the specifics of the proposed rules.

7.2 Further Development of the Single Laboratory Procedure

Recommendation that EPA Develop an Alternative to the Current 40 CFR Part 136 Appendix B Procedure

Although the Committee did not reach consensus on a procedure, we recommend that EPA act to develop an alternative to the current 40 CFR Part 136 Appendix B procedure. The results of the Pilot Study, and our evaluation of the DQ FAC Single Laboratory Procedure v2.4, indicate that there are deficiencies in the current 40 CFR Part 136 Appendix B procedure that can and should be corrected. The DQ FAC Single Laboratory Procedure v2.4 submitted contains elements that would be valuable to the agency in developing a new procedure.

Vote: 20 Agree, 0 Not Opposed, 0 Disagree

Approved By Consensus

Meeting #10, Decision 10.A

The purpose for this vote was to emphasize that the existing 40 CFR Part 136, Appendix B procedure does not meet the criteria or properties determined to be critical by the Committee. While the DQ FAC Single Laboratory Procedure v2.4 did not achieve full consensus, it was passed with a majority vote and has most, if not all, of the elements the Committee considers appropriate for a Part 136, Appendix B procedure. As EPA proceeds to amend 40 CFR Part 136, EPA will find the Committee's deliberations concerning the DQ FAC Single Laboratory Procedure v2.4 and results of the Pilot Study particularly helpful.

7.3 Additional Testing and Peer Review of the Single Laboratory Procedure

Post Committee Pilot of Proposed Procedure/s

The Committee recommends that EPA's Office of Water complete a follow up pilot study to confirm the performance of the procedure/s proposed for promulgation.

Vote: 17 Agree, 3 Not Opposed, 0 Disagree

Approved By Consensus

States: 3 Agree, 1 Not Opposed

Labs: 3 Agree, 1 Not Opposed

Industry: 4 Agree

Public Utilities: 3 Agree, 1 Not Opposed

EPA: 1 Agree

Environmental Community: 3 Agree

Meeting #10, Decision 5.E

Very early in the discussion of procedures it was agreed that the optimal detection or quantitation procedure might be a modification of one or more of the candidate procedures. Given this possibility, the Committee wanted to make it clear, if such an approach were recommended, that any procedure proposed for promulgation by EPA in the future should first be pilot tested to verify that it performed as desired.

The scope of the future pilot testing should be guided by the criteria delineated in the "What do we want a procedure to do" document adopted by the Committee. Because of the extremely tight time constraints of the previous pilot testing performed under the guidance of the Committee, it was not possible to test some of the long-term and verification aspects of certain procedures. Although the Committee encourages EPA to implement its recommendations as soon as practicable, this should not result in haste that would preclude careful testing of proposed procedures to assure they perform as required because it is anticipated that these procedures will be in use for decades to come.

Peer Review of the Proposed Procedure/s

The Committee recommends that a formal peer review of the Committee recommended procedure take place.

Vote: 16 Agree, 4 Not Opposed, 0 Disagree

Approved By Consensus

States: 3 Agree, 1 Not Opposed

Labs: 3 Agree, 1 Not Opposed

Industry: 4 Agree

Public Utilities: 3 Agree, 1 Not Opposed

EPA: 1 Agree

Environmental Community: 3 Agree

Meeting #10, Decision 5.H

Consensus on this recommendation was obtained before the Committee voted on the recommended procedure/s and was thus formulated based on the assumption that the Committee would recommend specific procedure/s. Although consensus on a procedure was not subsequently achieved, it was clearly the intent of the Committee that any procedure to be proposed should be submitted to a formal peer review.

7.4 Implementation of the New Regulations

Recommendation for EPA Development of Guidance and Outreach Materials for Stakeholders

The Committee recommends that EPA develop guidance and outreach materials for stakeholders as EPA implements the Committee recommendations.

Vote: 20 Agree, 0 Not Opposed, 0 Disagree

Approved By Consensus

Meeting #10, Decision 10.B

Recommendation for EPA Development of Guidance/Computer Applications for Determination of Detection and Quantitation Limits

The Committee recommends that EPA develop and implement guidance on the new procedures as well as a computer-based program to assist in calculating detection and quantitation limits.

Vote: 20 Agree, 0 Not Opposed, 0 Disagree

Approved By Consensus

Meeting #10, Decision 5.C

Implementation of the Committee recommendations represents a significant implementation challenge to EPA. A few of the many implementation issues EPA will need to consider include:

1. What should be the effective date of the new rules after promulgation? Laboratories will need time to familiarize themselves and become proficient with the new procedures and states may need time to make corresponding changes to their own regulations or guidance documents.
2. EPA will need to prioritize the creation of National Quantitation Limits, focusing on those analytes of most concern.
3. EPA will need to reach out to all parties, including its Regional offices, with guidance so that the new procedures and permitting schemes are well understood and can be implemented fairly. This will be especially challenging in the first years of the new program when EPA is essentially operating a dual system, one for analytes that do not have associated National Quantitation Limits, another for analytes with national Quantitation Limits. EPA needs to consider the most appropriate time for such guidance and some may need to be issued in parallel with the final rule.